## United States Environmental Protection Agency Region 4



# EVERGLADES ECOSYSTEM ASSESSMENT (PHASE IV REMAP)

## Quality Assurance Project Plan 9/19/2013

SESD Project Number: 13-0513

Prepared by

United States Environmental Protection Agency Region 4

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#### **FOREWARD**

This document is the Quality Assurance Project Plan (QAPP) for environmental data operations performed by the United States Environmental Protection Agency (EPA) Region 4 as part of the Everglades Ecosystem Assessment Phase IV Regional Environmental Monitoring and Assessment Program (REMAP). The Program investigates environmental stressors such as mercury, phosphorus, sulfur and water management in the Everglades ecosystem. This document follows EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations (EPA QA/R-5; USEPA 2001).

This QAPP is presented in three phases: planning, implementation and assessment. The first phase involved the development of Data Quality Objectives (DQOs), which provided statements about the expectations and requirements of the various data users. In the second phase, the QAPP and its associated documentation translate these requirements into measurement performance specifications and quality assurance/quality control (QA/QC) procedures for the data suppliers to provide the information needed to satisfy the data user's needs. Once the data have been collected and validated in accordance with the elements of the QAPP, the data will be evaluated to determine whether the DQOs have been satisfied. In this assessment phase, the data will be analyzed to determine whether they meet the assumptions made during planning and whether the total error in the data is small enough to support decisions within tolerable decision error rates expressed by the data users. Plans for data validation and assessment of the data are discussed in the final sections of the QAPP.

This QAPP follows organizational consistency and content of the current EPA guidance for such documents (USEPA 2001). In addition, this document has been prepared under EPA Region 4 jurisdiction and will be reviewed and approved prior to implementation of the 2013 sampling elements of the project.

This QAPP documents how QA/QC activities will be planned and implemented. Overall, the QAPP provides detail to demonstrate the following:

- The project's technical and quality objectives are identified and agreed upon.
- The intended measurements or data acquisition methods are consistent with project objectives.

- The assessment procedures are sufficient for determining if data of the type and quality needed and expected are obtained.
- Limitations on the use of the data can be identified and documented.

Project documents that have been prepared prior to the QAPP (e.g., project study plan, standard operating procedures (SOPs)) are appended or, in some cases, incorporated by reference.

The elements of this QAPP are categorized into "groups" according to their function and include the following:

### Group A: Project Management

This group of QAPP elements covers the general areas of project management, project history and objectives, and roles and responsibilities of the participants. The following elements ensure that the project's goals are clearly stated, that all participants understand the goals and the approach to be used, and that project planning is documented:

- Title and Approval Sheet,
- Table of Contents and Document Control Format,
- Distribution List.
- Project/Task Organization and Schedule,
- Problem Definition/Background,
- Project/Task Description,
- Quality Objectives and Criteria for Measurement Data,
- Special Training Requirements/Certification, and
- Documentation and Records.

### Group B: Measurement/Data Acquisition

This group of QAPP elements covers the aspects of measurement system design and implementation so that appropriate methods for sampling, analysis, data handling and QC are employed and will be documented. These elements are primarily contained in attachments to the OAPP:

- Sampling Process Design (Experimental Design);
- Sampling Methods Requirements;
- Sample Handling and Custody Requirements;
- Analytical Methods Requirements;

- Quality Control Requirements;
- Instrument/Equipment Testing, Inspection, and Maintenance Requirements;
- Instrument Calibration and Frequency;
- Inspection/Acceptance Requirements for Supplies and Consumables; and
- Data Management.

#### Group C: Assessment/Oversight

The purpose of assessment is to ensure that the QAPP is implemented as prescribed. This group of QAPP elements addresses the activities for assessing the effectiveness of the implementation of the project and the associated QA/QC activities:

- Assessments and Response Actions, and
- Reports to Management.

#### Group D: Data Validation and Usability

Implementation of Group D elements ensures that the individual data elements conform to the specified criteria, thus enabling reconciliation with the project's objectives. This group of elements covers the QA activities that occur after the data collection phase of the project has been completed:

- Data Review;
- · Validation and Verification;
- Reconciliation with Data Quality Objectives.

The organizational group performing the work is also responsible for implementing the approved QAPP. This responsibility includes ensuring that all personnel involved in the work have copies of or access to the approved QAPP along with all other necessary planning documents. In addition, the group must ensure that these personnel understand their requirements prior to the start of data generation activities.

Moreover, these organizations are responsible for keeping the QAPP current when changes to technical aspects of the project change. QAPPs must be revised to incorporate such changes and must be re-examined to determine the impact of the changes. Any revisions to the QAPP must be re-approved and distributed to all participants in the project.

#### SECTION A. PROJECT MANAGEMENT

#### A1. TITLE AND APPROVAL SHEET

Title: Quality Assurance Project Plan - Everglades Ecosystem Assessment (Phase IV

REMAP)

Organization: USEPA Region 4

Approvals:

**Project Personnel** 

Signature

Date

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#### A3.1 LIST OF ABBREVIATIONS

AFDW - Ash Free Dry Weight

ANOVA - Analysis of Variance

ASB - Analytical Support Branch

BD - Bulk Density

C - Carbon

CERP - Comprehensive Everglades Restoration Plan

Chla - Chlorophyll a

CH<sub>4</sub> - Methane

Cl - Chloride

CCV - Continuing Calibration Verification

CO<sub>2</sub> – Carbon Dioxide

COR - Contract Officer Representative

DOC- Dissolved Organic Carbon

DQO - Data Quality Objective

DQA - Data Quality Assessment

EAB - Ecological Assessment Branch

EDD - Electronic Data Deliverable

ENP - Everglades National Park

EPA - Environmental Protection Agency

ESAT - Environmental Services Assistance Team

FIU/SERC - Florida International

University, Southeast Environmental Research Center

g - gram

g/cc - gram per cubic centimeter

Hg - Mercury

H2S - Hydrogen Sulfide

MC - Mineral Content

MDL - Method Detection Limit

MeHg – Methyl Mercury

MQL - Method Quantification Limit

mg/L - milligrams per liter

mg/kg - milligram per kilogram

mm - millimeter

mV - millivolt

N - Nitrogen

NELAC - National Environmental Laboratory Accreditation Conference

NH<sub>4</sub> - Ammonia

NO<sub>2</sub> - Nitrite

NO<sub>3</sub> - Nitrate

NTU - Nephlometric Turbidity Unit

OQA - Office of Quality Assurance

P - Phosphorus

PE - Performance Evaluation

ppb - parts per billion

ppm - parts per million

PO<sub>4</sub> - Phosphate

PQL - Practical Quantification Limit

QAPP - Quality Assurance Project Plan

QAQC - Quality Assurance Quality Control

REMAP - Regional Environmental

Monitoring and Assessment Program

RPD - Relative Percent Difference

RSD - Relative Standard Deviation (coefficient of variation)

SU - Standard Units

SESD - Science and Ecosystem Support Division

SO<sub>4</sub> - Sulfate

SOP - Standard Operating Procedure

SRM - Standard Reference Material

TC - Total Carbon

TMDL - Total Maximum Daily Load

THg - Total Mercury

TN - Total Nitrogen

TP – Total Phosphorus

TPO - Technical Project Officer

TSA - Technical Systems Audit

WCA – Water Conservation Area

WPD - Water Protection Division

μg/kg - microgram per kilogram

μg/cc - microgram per cubic centimeter

μg/L - microgram per liter

## A4. PROJECT TASK ORGANIZATION

#### A4.1 Purpose/Background

The purpose of the project task organization is to provide involved parties with a clear understanding of the role that each plays in the project and to provide lines of authority and reporting.

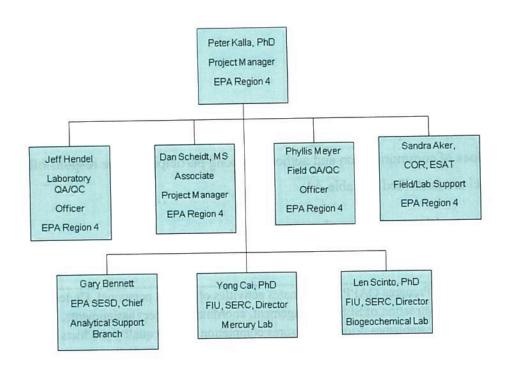
## A4.2 Roles and Responsibilities

This section describes the overall organization for the project, along with duties and responsibilities of project personnel. The project organizational chart is shown in Figure A.1 and includes the lines of communication and authority among participants. The responsibilities of these personnel are described in Table A1.

Table A1. Key position and areas of responsibility.

TITLE	DUTIES/RESPONSIBILITIES
EPA Project Manager	Prepares QAPP. Coordinates activities of project personnel. Under direction of SESD management, coordinates project assignments, establishes priorities, ensures completion of high quality products on-time and under budget, implements corrective actions including those recommended by the project lab and field QA Officers, reviews and provides project deliverables, interacts with clients and funding entities, assures that technical requirements are met in accordance with data quality objectives. SESD Management has responsibility for implementation of corrective actions.
EPA Associate Project Manager	Assists Project Manager with all of the above as needed. Provides project link to data users. Represents interests of Water Protection Division.
Field QA Officers	Responsible for oversight of field sampling efforts with strict adherence to project SOPs and QAPP. Oversees field data collection and sample collection. Reports deficiencies or necessary corrections to the Project Leader. Due to the length of the field deployment this role will be assigned daily to a qualified on-site individual by the Project Manager.
Project Lab QA Officer	Performs oversight of all analytical labs for the project. Reviews all lab SOPs and analytical methods for appropriateness in meeting data quality objectives. Coordinates performance audits. Performs lab on-site audits. Provides on-site FIU lab QA oversight during sampling efforts. Reports deficiencies or necessary corrections to the Project Leader.
EPA Region 4 QA Officials	Reviews and approves the QAPP. Commits staff for performing the work in support of this study.

Figure A1. Project Organizational Chart



## A5. PROBLEM DEFINITION/BACKGROUND

## A5.1 Purpose and Organization

The purpose of this project is to characterize the magnitude and extent of mercury contamination, cultural eutrophication, hydroperiod modification and macrophyte species invasion in the freshwater Everglades ecosystem. A related purpose of the project is to assess the risks to fish and wildlife from these environmental stressors. Phosphorus and mercury data resulting from the project will likely be used to inform compliance decisions. Mercury data will also likely be used for risk assessments and to calculate Total Maximum Daily Loads (TMDLs). Project personnel have been selected based on their performance and extensive experience, and are organized to ensure accountability for the quality of data produced.

## A5.2 Problem Statement and Background

#### Background

Everglades environmental threats: During the last century, human impacts on the Everglades ecosystem have become apparent. The historic sheet flow of surface water has been altered by a highly managed system of canals, levees and water control structures. Altered hydrology has impacted plant communities and wading bird populations. Canals have become inadvertent conduits for the transport of nutrients and other pollutants from agricultural and urban areas into the Everglades, resulting in eutrophication. The Everglades no longer receives the proper quantity or quality of water at the right places or at the right times. The remnant Everglades no longer exhibits the water regimes, vast area, and mosaic of oligotrophic habitats that defined the pre-drainage ecosystem. As human population continues to increase, conflicts between the natural system, agriculture and urban areas can be expected to intensify. Although one-third of the 16,000 square mile Everglades watershed is in public ownership, there are many environmental issues, often inter-related, that must be resolved in order to protect or restore the Everglades ecosystem. These include water management; water supply conflicts; soil loss; water quality degradation and eutrophication; mercury contamination of gamefish, wading birds and the Florida panther; habitat alteration and loss; protection of endangered species; and introduction and spread of nuisance exotic species.

CERP: During the 1990s an ambitious Comprehensive Everglades Restoration Plan (CERP) was initiated by the state and federal governments. The intent of CERP is to provide the right amount of water and the right flow conditions for the Everglades and other natural areas in south Florida while simultaneously providing the urban and agricultural water and flood control needs for the next 50 years. As a result, the Everglades should experience a more natural timing, flow, quantity and quality of water resulting in a diverse and natural habitat for plants and animals. Major CERP projects initially included removal of canals and levees, operational changes in water management, construction of 300 aquifer and storage wells, establishment of 180,000 acres of above ground water storage reservoirs, and construction of about 36,000 acres of wetlands to be managed for water quality treatment. As of 2000, a total of 65 individual projects were proposed at an estimated cost of about \$8 billion. Adaptive assessment and monitoring are important aspects of CERP. An extensive monitoring and assessment plan has been developed that describes in detail the monitoring components and supporting research (CERP 2004).

In October 2011, the intergovernmental South Florida Ecosystem Restoration Task Force endorsed a state-federal initiative to accelerate planning for key restoration projects in the heart of America's Everglades. The Central Everglades Planning Project (CEPP) provides a plan for a suite of restoration projects in the central Everglades to prepare for congressional authorization as part of CERP. The focus of CEPP is increasing the flow of water to be directed south to the central Everglades, Everglades National Park and Florida Bay while protecting coastal estuaries.

Mercury contamination and controls: In 1989, a Florida panther (an endangered species) was found dead in Everglades National Park with its death attributed to mercury toxicosis. Since then, over 2 million acres of the Everglades have been placed under fish consumption advisories to protect human health from mercury contamination. Risk assessments indicate that wading birds in the central Everglades are at increased risk due to mercury contamination. During the 1990s, Florida initiated efforts to control mercury by placing regulatory controls on air emissions. Recent data indicate a drop in mercury in largemouth bass and wading birds in portions of the Everglades. However, fish consumption advisories remain in effect (Axelrad et al. 2013).

Phosphorus enrichment and controls: The Everglades has been subjected to phosphorus pollution since the 1960s. Interior Everglades marshes that are distant which are physically isolated from anthropogenic nutrient sources have extremely low total phosphorus (TP) concentrations in surface water, reaching as low as the method detection limit of 2 parts per billion (ppb). Phosphorus loading in stormwater from the Everglades Agricultural Area (EAA) and urban areas has significantly increased phosphorus concentrations in the downstream Everglades (to greater than 100 ppb), causing eutrophic impacts to these oligotrophic wetlands. Among the progressive eutrophic impacts are loss of the natural communities of algae and periphyton that are defining characteristics of the Everglades; decreased water column dissolved oxygen; increased soil phosphorus content; conversion of the native wet prairie-sawgrass mosaic to woody species or dense single-species stands of cattail with no open water; and consequent loss of wading bird foraging habitat. These collective changes impact the structure and function of the aquatic ecosystem. By 1990, South Florida Water Management District and U. S. Fish and Wildlife Service reported that about 30,000 acres of the public Everglades within WCA2A and the Refuge were impacted (LOTAC II, 1990).

In 2005, Florida adopted and EPA approved a 10 ppb water quality criterion for TP in the Everglades in order to prevent nutrient-induced imbalances in natural populations of aquatic flora or fauna. The criterion is applied as a long-term average, with achievement of the criterion within the Everglades waterbody determined by data collected monthly at fixed long-term marsh sampling locations. During the 1990s, Florida initiated regulatory efforts to control phosphorus. As of 2013, about 60,000 acres of constructed wetlands, called Stormwater Treatment Areas (STAs), have been built (at a cost of about \$1 billion) to remove phosphorus from agricultural and urban stormwater prior to discharge into the Everglades. Agricultural Best Management Practices (BMPs) began in the EAA in 1994, with a goal of removing 25% of the phosphorus load delivered to the Everglades. These BMPs have consistently reduced the TP load by more than 25% (higher than 70% in some years) as compared to the load that would have been expected had the BMPs not been in place (Baker, Madden and Wade 2013).

While these efforts greatly reduced phosphorus loading into the Everglades, inflow concentrations remained above 10 ppb. Consequently, in 2012 EPA reached a historic agreement in revised STA National Pollutant Discharge Elimination System (NPDES) permits and Consent

Orders that include a protective Water Quality Based Effluent Limit (WQBEL) that is equivalent to the 10 ppb criterion, about \$900 million of flow equalization basins and STA expansions to store and treat water, requirements for a robust monitoring and research plan to confirm that restoration is moving forward, and an enforceable compliance schedule with project completion dates of 2018 to 2025.

The EEA project: In 1992 the EPA Region 4 Science and Ecosystem Support Division (SESD) was charged by the Regional Administrator to develop an action plan to evaluate the mercury issue and provide a scientific basis for evaluating options and strategies to eliminate mercury contamination in the Everglades ecosystem. Subsequently, SESD prepared a research plan, had this plan peer-reviewed, and initiated the study in 1993 as a Regional Environmental Monitoring and Assessment Program (REMAP) Project. This Project is also referred to as the Everglades Ecosystem Assessment (EEA) Project. From 1993 to 1995, about 200 canal locations were sampled throughout the Everglades, Big Cypress and the Everglades Agricultural Area (EAA). In 1995-1996 and 1999, phases I and II of the Everglades marsh sampling, respectively, were conducted with sampling completed at about 750 locations. In 2005, Phase III was completed with sampling at 228 Everglades marsh locations.

The Everglades Ecosystem Assessment Project simultaneously addresses the multiple environmental issues described above, and indicators measured by this Project will permit answers to questions regarding these multiple environmental issues. A central goal of the Project is to answer assessment questions related to the magnitude, extent, trends and transformation processes in mercury contamination of the Everglades ecosystem. Mercury is used as an example in the DQO process described in Appendix 1. However, the same DQO process will be applied to other indicators in the project such as phosphorus and sulfur.

#### A6 PROJECT/TASK DESCRIPTION AND SCHEDULE

#### A6.1 Purpose/Background

The purpose of Phase IV is to provide decision makers with data so that improved environmental decisions can be made on the multiple environmental issues and restoration efforts being conducted in South Florida. Phase IV is an extension of the Phase I, II & III Assessments conducted from 1994 through 2005. Project data collected during Phases I - III

have been requested and used for many purposes by over 30 state or federal agencies, Indian tribes, university scientists, non-governmental organizations and private consultants. The Project has resulted in over 20 scientific journal publications or agency reports, and has been cited in over 200 journal publications. It is expected that Phase IV phosphorus and mercury data collected by this project will be used by state and federal agencies for regulatory purposes. General project data uses include:

- Assessing phosphorus conditions, spatial patterns and temporal trends throughout the Everglades Protection Area. Assessing the effectiveness of phosphorus regulatory programs.
- Assessing mercury conditions, spatial patterns and temporal trends throughout the Everglades Protection Area. Assessing the effectiveness of mercury regulatory programs.
- Assessing sulfur conditions, spatial patterns and temporal trends throughout the Everglades Protection Area.
- Assessing water quality, hydrologic and ecological conditions throughout the Everglades Protection Area and determining the effects of CERP hydrologic or water quality modifications.
- Assessing the comparative risks to the Everglades Protection Area of various stressors such as eutrophication, mercury contamination and hydrologic modification.

Some specific project data uses have included the following:

- Phosphorus used in model to predict Everglades' response to water management and P control (Florida DEP, SFWMD).
- Soil phosphorus data used to define P-impact portions of the Everglades and determine applicability of the 10 ppb water quality criterion as required by Florida law (Florida DEP).
- Phosphorus data used in Everglades phosphorus gradient model to predict Everglades' response to P enrichment from upstream P sources (SFWMD, USACE).
- Mercury data used as model input in marsh mercury cycling model and for draft TMDL development (USEPA ORD, TetraTech).
- Mercury data used in risk assessments for Everglades wading birds (SFWMD, TetraTech).
- Mercury data used by Florida and U. S. Army Corps of Engineers in Environmental Impact Statements for Stormwater Treatment Areas constructed to control phosphorus (USACE, SFWMD).
- Mercury and water quality data used to develop empirical models of aquatic cycling to define mercury, carbon, sulfur, phosphorus and oxygen inter-relationships (USGS, TetraTech, USEPA Region 4).
- Water depth data used to update surface water management models used for Everglades hydrologic restoration (SFWMD).

 Mercury data used to develop Everglades mass balances for total mercury and methyl mercury (EPA, FIU).

Project results have been published in Stober et al. 1999, Stober et al. 2001 and Scheidt and Kalla 2007. Phase III results reported in Scheidt and Kalla (2007) include the following:

Mercury contamination -- declining in mosquitofish, but still elevated: The overall mercury concentration in mosquitofish, a key prey fish for Everglades gamefish and wading birds, dropped markedly from 1995-1996 to 1999 and from 1999 to 2005. However, during the 2005 wet season approximately 65% of the marsh exceeded 77 ppb, a concentration EPA has recommended in trophic level 3 fish as being protective of top predators such as birds and mammals. Fish mercury was highly correlated with mercury in forms of periphyton, but not with mercury in surface water. The highest concentrations continue to be observed in Water Conservation Area (WCA) 3 and Everglades National Park (the Park), as was the case in 1995-1996.

Mercury contamination -- bioaccumulation varies greatly over space: The bioaccumulation of mercury from the water column to mosquitofish varies spatially by a factor of approximately 10 throughout the Everglades. The highest concentrations of methylmercury and total mercury in surface water generally occur in WCA 2 and parts of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (the Refuge) - areas that do not have high mercury in mosquitofish. An inhibitory mechanism may explain the lack of bioaccumulation in these waters. Significant, negative correlation coefficients were found between bioaccumulation and surface water dissolved organic carbon, porewater sulfide and porewater sulfate.

Mercury contamination -- slight changes in water: Program data indicate that there was a small decrease in the concentration of methylmercury in surface water in the wet season in 2005 as compared to the wet season in 1995. Conversely, there was a slight increase in the concentration of total mercury in surface water in the wet season in 2005 as compared to 1995. This parameter had a median of 2.0 parts per trillion for the duration of the Program, well below the Everglades' water quality criterion of 12 parts per trillion. Attainment of the criterion for surface water has not prevented bioaccumulation to unacceptable levels in prey fish.

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<u>Phosphorus enrichment</u>: During 2005 soil phosphorus exceeded 500 milligrams per kilogram (mg/kg), Florida's definition of "impacted", in 24% of the Everglades, and it exceeded 400 mg/kg, CERP's restoration goal, in 49% of the Everglades. These proportions are higher than the 16% and 34%, respectively, observed in 1995-1996.

Sulfate enrichment: About 57% of the Everglades marsh had a surface water sulfate concentration exceeding 1.0 parts per million (ppm), CERP's restoration goal. This contrasts with 66% observed in 1995. During November 2005 surface water sulfate was about 90 ppm in WCA 2, well above marsh background of < 1.0 ppm. Interior portions of the Everglades distant from stormwater discharges from the Everglades Agricultural Area had concentrations < 1.0 ppm, although elevated concentrations were still found as far south as Shark Slough within the Park. The surface water sulfate concentration in the Everglades overall during the wet season showed a decrease from 1995-1996 to 2005.

Pronounced water quality gradients: There are clear spatial gradients in surface water phosphorus, sulfate, organic carbon, nitrogen, chloride and conductivity in the Everglades marsh. These gradients are due to the relative contribution of rainwater, stormwater and groundwater. The highest concentrations typically occur during the wet season in WCA 2 as compared to the dry season, due to its proximity to the Everglades Agricultural Area and stormwater discharges. Concentrations progressively decrease downstream. Location, time of year and water management practices are important factors that affect water quality.

Soil loss in the public Everglades: The Program previously found that from 1946 to 1996, about one-half of the peat soil was lost from approximately 200,000 acres of the public Everglades that had been subjected to drier conditions. No overall change in soil depth was observed from 1996 to 2005. About 25% of the Everglades overall has 1.0 feet or less of soil, as does 53% of the Park. Water management must be improved to maintain the remaining marsh soils if the plant communities and wildlife habitat of these wetlands are to be preserved. The northern portion of WCA 3 must be rehydrated if further soil loss is to be prevented. Rehydration of this area is a goal of CEPP.

Ecological condition varies by location and time: The condition of the Everglades varied greatly with location. Rainfall-driven portions of the system that are distant from the influence of

canal water, such as the interior of the Refuge and the southwest portion of WCA 3, were found to have better water quality and low soil phosphorus. In contrast, northern WCA 3 had poorer water quality, thinner soil due to water management practices, elevated soil phosphorus and extensive cattail encroachment. WCA 2 had phosphorus enrichment and cattail encroachment, along with high sulfate, organic carbon, nitrogen, chloride and conductivity in surface water.

### A6.2 Description of the Work to be Performed

Standard field measurement, sampling, and laboratory analytical protocols that are likely to be used during the course of the project are found in Tables 1, 2 and 3. Additional sampling protocols developed for specific use during this project are provided in Appendix 2 or the FIU Plan of Study (Appendix 5). The following have been identified for the project:

- Special personnel and equipment requirements.
- The assessment techniques needed.
- Project and quality records required, including various reports needed. Field data will be
  entered into an Excel spreadsheet by project personnel on-site at the FIU staging area.
  Data entries will be verified by a second individual. Analytical labs will provide data and
  data packages, including routine analytical QC, in electronic format to the Project Lab
  QA Officer. Original copies of all field data sheets, chain of custody records, data
  packages and QA/QC records will be kept at SESD in accordance with the Control of
  Records SOP.

#### A6.3 Schedule

May/August 2013

On-site lab audits

July 2013

Field method pilot study

Prior to Sept 23

QAPP approval

September 23 - October 11

Wet season sampling

December 1, 2013

Wet season data packages

May 2014

Data validation

October 2015

Project final report

## A7. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

The purpose of this element is to document the data quality objectives (DQOs) of the project and to establish performance criteria for the mandatory systematic planning process and

measurement system that will be employed in generating the data. DQOs were prepared during the Phase I, II & III Assessments (Appendix 1). Sampling and analytical methods criteria specified under the elements contained in Section B are designed to meet the applicable criteria described in the DQO document. To quantify analytes across the entire ecosystem, MDL/MQL/PQLs are specified to meet the minimum concentrations either found in previous phases or taken from the scientific literature (Table 2). For critical parameters such as mercury and phosphorus, specified values are lower than levels established as water quality standards.

## A8. SPECIAL TRAINING REQUIREMENTS/CERTIFICATION

Laboratories (FIU, EPA) performing analyses for parameters of regulatory interest, such as phosphorus, sulfur and mercury, are NELAC-accredited or ISO 17025 accreditation.

Sampling locations within the 2000-square mile study area will be accessed via helicopter. Field personnel received helicopter safety training at SESD in June 2013 by the U. S. Department of Interior Office of Aircraft Services. SESD management maintains all training records.

Special equipment includes specialized sampling equipment for marsh bottom water collection, a vacuum chamber used to sample surface water, clean methods for surface water ultra trace level mercury sampling, and Global Positioning System equipment for navigation to and logging station locations. Primary and backup field sampling personnel either have experience or have been trained in the operation of all equipment. Final training sessions were held in August 2013 at SESD. Personnel will be provided with final written protocols at the initiation of field sampling. Sampling within Arthur R. Marshall Loxahatchee National Wildlife Refuge, Everglades National Park, Big Cypress National Preserve and the Miccosukee Tribe of Indians of Florida's Federal Reservation all require sampling permits from the U. S. Fish and Wildlife Service, National Park Service, or the Miccosukee Tribe, respectively. South Florida Water Management District has indicated that a sampling permit is not required for Everglades Water Conservation Areas 2 and 3.

A job hazard analysis and project safety plan (Appendix 4) have been developed for the project. Daily safety briefings on helicopter operations will be conducted by the pilot.

#### A9. DOCUMENTATION AND RECORDS

#### A9.1 Purpose/Background

This element defines which records are critical to the project and what information needs to be included in reports, as well as the data reporting format and the document control procedures to be used. Required report formats are also discussed in Section D. Specification of the proper reporting format, compatible with data validation, will facilitate clear, direct communication of the project. Relevant SESD SOPs (Table 1) will be followed.

#### **A9.2 Project Information Requirements**

#### A9.2.1 Field Operation Records

<u>Sample Collection Record</u>: To document that the proper sampling protocols were followed in the field. At a minimum, this documentation will include the names of the persons conducting the activity, sample date and time, sample number, sample collection points, maps and diagrams, equipment/method used, climatic conditions, and unusual observations as applicable. Field notebooks are used to record raw data and make references to prescribed procedures and changes in planned activities.

<u>Chain-of-Custody Records</u>: To document the progression of samples as they travel from the original sampling location to the laboratory and finally to their disposal area, if applicable. Chain-of-custody forms will be required for all environmental samples.

QC Sample Records: To document the generation of quality control (QC) samples such as field, (equipment) blank and duplicate samples. Documentation of sample integrity and preservation along with calibration and standards traceability documentation capable of providing a reproducible reference point will be required for appropriate QC records. Quality control sample records will contain information on the frequency, conditions, level of standards and instrument calibration history.

General Field Procedures: To document general field conditions and actions and outline potential areas of difficulty in gathering specimens. Field logs will be completed to address this documentation.

<u>Corrective Action Reports</u>: Corrective action reports to show what methods were used in cases where general field or laboratory practices or other standard procedures were not followed and include the methods to resolve the issue. The Project Leader is responsible for corrective actions in the field.

#### A9.2.2 Laboratory Records

Sample Data: Documentation of the times that samples were analyzed to verify that they met the holding times prescribed in the analytical methods. Included will be the overall number of samples, sample location information, any deviations from the SOPs, time of day and date. Corrective action procedures to replace samples violating the protocol also will be documented.

Sample Management Records: Sample management records document sample receipt, handling and storage, and scheduling of analyses. The records verify that the chain-of-custody and proper preservation were maintained, reflect any anomalies in the samples (such as receipt of damaged samples), note proper log-in of samples into the laboratory, and address procedures used to ensure that holding time requirements were met.

Test Methods: Analyses to be performed are described in the Phase IV plan of study (Appendix 5) and in Tables 2 and 3. SOPs for the analytical labs (Table 1) describe how the analyses will be carried out in the project laboratories, including sample preparation and analysis, instrument standardization, detection and reporting limits, and test-specific QC criteria. Documentation demonstrating laboratory proficiency with each method used is included or is available for inspection.

QA/QC Reports: These reports will include the general QC records, such as initial demonstration of capability, instrument calibration, routine monitoring of analytical performance and calibration verification. Project-specific information from the quality assurance/quality control (QA/QC) checks such as blanks, spikes and calibration check samples, will be included in these reports to facilitate data quality analysis.

#### A9.2.3 Data Handling Records Documentation

The protocols and actions used in data reduction, verification, and validation are provided below and in Section D of this QAPP. Data reduction addresses data transformation operations

such as converting raw data into reportable quantities and units, use of significant figures, recording of extreme values and blank corrections. Data verification ensures the accuracy of data transcription and calculations, if necessary, by checking a set of computer calculations manually. Data validation ensures that QC criteria have been met.

## A9.3 Data Reporting Package Format and Documentation Control

The format of data reporting packages will be consistent with the requirements and procedures used for data validation and data assessment described in Sections B, C, and D of this QAPP. Individual records that represent actions taken to achieve the objective of the data operation and the performance of specific QA functions are potential components of the final data reporting package.

#### A9.4 Data Reporting Package Archiving and Retrieval

Data reporting packages will be submitted to the Project Lab QA Officer within 60 days of sample collection. Data packages will be maintained at SESD by the Project Manager until the end of the study, and then will be maintained in the Project File in the SESD Records Room as per the Control of Records SOP. The laboratories will keep all documentation related to the data reporting package and preparation and analysis of samples on file for a minimum of 5 years. If the laboratory desires to dispose of these records after 5 years they will first contact the laboratory QA/QC project officer. That person may request that the documents be forwarded to EPA.

#### A9.5 Disposition of Records and Documents

All study documentation (field sheets, lab data packages, instrument calibration records, chain of custody forms, digital photos, electronic data files, etc.) will be stored in the SESD Records Room as per the Control of Records SOP and EPA records management policy.

## SECTION B. MEASUREMENT/DATA ACQUISITION

## BI SAMPLING PROCESS DESIGN (EXPERIMENTAL DESIGN)

#### **B1.1** Purpose/Background

This section provides information to describe how and why the samples will be collected. The following have been identified for the project:

- a schedule for project sampling activities,
- a rationale for the design (in terms of meeting DQOs),
- · the sampling design assumptions, and
- · the procedures for locating and selecting environmental samples.

The September 2013 wet season sampling effort will involve sampling 125 marsh locations (63 new sites and 62 revisited sites from 2005) in the public Everglades. Media to be sampled include surface water, bottom water, sediment, floc, periphyton, sawgrass, and mosquitofish (Tables 2 and 3). Sample locations are provided in Table 5 and Figures 2a and 2b. The probability design used to sample the Everglades marsh in Phases I - III was developed from the EMAP base grid in order to ensure spatial coverage. The design includes stratification by the four major subareas of the system (ENP, the Refuge, and the Water Conservation Areas (WCA2 and WCA3)) to ensure that coverage of smaller subareas is adequate for obtaining variance estimates. A consistent sample size of approximately 125 random points per seasonal survey ensures acceptable confidence intervals around estimated environmental parameters. This design criterion is compatible with logistical considerations allowing helicopter-supported crews to complete all sampling in about 16 days, which also matches throughput capacities of cooperating analytical laboratories. This approach produces quantitative statements with known confidence about environmental condition across the entire population over space and time; for example, that the proportion of the Everglades having a total phosphorus concentration greater than 400 mg/kg (the CERP goal) in soil in 2005 was  $49.3 \pm 7.1$  %, and that this proportion is statistically significantly greater than the  $33.7 \pm 5.4$  % measured in 1995-1996.

EPA's Office of Research and Development (ORD) Western Ecology Division National Health and Environmental Effects Research Laboratory provided the statistical design and sample draw. The 2013 statistical design is a probability survey design that consists of two parts: a) 50% of the sites are a probability subsample of the prior survey design (2005) and b)

50% of the sites are a new probability sample. Since the two designs are completed independently, the combined survey design is also a probability survey design. The combined design has two objectives. The first objective is to estimate the current status as has been done in the past. The second objective is to estimate change between the two time periods (2005 and 2013). ORD has determined that the power of detecting a change is increased by visiting 50% of the sites in both time periods. ORD simulation studies of alternative designs for estimating change favor survey designs where approximately 50% of the sites are visited in both time periods. The change estimation is based not only on the panel of 50% sites visited twice but also on the panel of sites from the first time period (2005) and on the panel of sites from the current time period (2013). Classification of measurements as being critical versus non-critical was performed at a Technical Team meeting held at EPA Region 4 offices. Measurements known to have water quality criteria or regulatory implications or usage are considered "critical" measurements. The critical parameters are mercury, sulfur (in the form of sulfate and sulfide), and phosphorus, along with a few other water quality parameters that have Florida surface water quality criteria. All other measurements collected during the project are considered non-critical and useable for research purposes.

#### **B2 SAMPLING METHODS REQUIREMENTS**

## **B2.1** Sample Collection, Preparation, and Contamination Prevention Procedures

A biogeochemical/water sampling crew will access the sampling locations via helicopter. The protocol for locating sample stations is described in Appendix 3. Two helicopters will operate simultaneously so that 125 stations can be sampled throughout the Everglades Protection Area within a 20-day period, beginning September 23 at the southern end of Everglades National Park and moving northward toward the Arthur R. Marshall Loxahatchee National Wildlife Refuge. Each crew will be comprised of three USEPA employees. One helicopter will have a fourth person who is a plant expert from Florida International University. If it is not possible to sample 125 stations within the 20 days, contingencies will be developed in coordination with DOI.

Aircraft personnel will operate under DOI requirements for safety, flight following, ship inspection, personal protective equipment and pilot carding. DOI is arranging for two helicopters with fixed floats for the duration of the sampling effort, and pilots. Field crews will measure in-

situ water chemistry (pH, turbidity, specific conductivity, dissolved oxygen, temperature) with a properly calibrated YSI water quality sonde. They will collect surface water, sediment, floc, periphyton, sawgrass and mosquitofish for laboratory analysis. Each sampling site will be documented with digital photography.

Project sampling, preservation, preparation and documentation protocols are included in the EPA SESD Standard Operating Procedures. These are identified in Table 1, with project-specific methods identified in Appendix 2. The project DQOs were considered in choosing or revising these methods to ensure that (1) the sample accurately represents the portion of the environment to be characterized, (2) the sample is of sufficient volume to support the planned chemical analysis, and (3) the sample remains stable during shipping and handling. EPA, Environmental Services Assistance Team (ESAT) and Southeast Environmental Research Center (SERC) personnel will provide technical support for sampling activities associated with the project.

Field personnel will follow EPA Method 1669 (Clean hands/dirty hands for trace-level mercury), with the following modifications. Both surface water samplers will wear shoulder-length gloves, in lieu of wind suits, since a vacuum chamber is used for the project instead of direct dipping. Modifications from the SESD Operating Procedure for Surface Water Sampling will occur for this project as follows. Nitrile gloves will be used by samplers who are allergic to latex and prefer a tight-fitting glove. Samplers desiring greater dexterity will put on the short glove over the shoulder-length glove.

Field personnel will not enter the water while collecting water samples in order to avoid disturbing the water column. Water samples will be collected from the helicopter float utilizing a vacuum chamber and filter screen assembly. Water samples will be screened during collection to ensure that floc, sediment and periphyton will be kept out. The vacuum chamber will hold the sample bottle inside an airtight acrylic, cylindrical chamber with an o-ring sealed lid. The chamber is connected via Teflon® sample tubing to a rigid Teflon® extension pole that provides extended reach for the samplers. The extension pole is capped at the surface water intake with a magnetic screen holder. A clean, two inch square of 100 µm Nitex® screen will be placed inside the magnetic screen holder prior to collecting each sample to prevent debris from entering the

sample. A hand vacuum pump will draw the surface water into the sample bottle through the screen and tubing.

Field sampling equipment will be rinsed with ambient site water before each station is sampled to prevent cross contamination from the previous station. All sample containers will have been tested for relevant contaminants prior to use, as described in SESD SOP Purchasing of Services and Supplies (Table 1).

#### **B2.2** Support Facilities for Sampling Methods

The Florida International University Southeast Environmental Research Center wetland soils biogeochemistry laboratory in Miami, Florida will serve as the staging area for all field operations. Project operations that will be coordinated out of this facility include but are not limited to field equipment calibration, sample container preparation, data downloading for GPS equipment, downloading site digital photos, sample storage, sample shipping to the project analytical labs and chain of custody documentation, and sulfide analysis.

## **B2.3** Sampling/Measurement System Response and Corrective Action Process

The field leadership team will consist of sampling crew members, crew chiefs, the Field QA Officer and the Project Managers (in order of increasing responsibility). When deviations from approved standard operating procedures (SOPs) occur, or in situations when sample integrity is compromised or questionable, it will be the responsibility of the crew member who identified the issue to bring it to the immediate attention of the crew chief for attempted resolution. In the event of an instrument problem, it will be the responsibility of the operator to try to correct the problem (e.g., recalibrate the instrument). If the problem persists or cannot be identified, the issue will be brought to the attention of the crew chief for resolution. Issues will be taken up the chain of leadership, while the crew is on station if possible, until they are resolved. All issues and their resolution will be documented by the Field QA Officer and approved by the Project Manager. Corrective actions for field activities will be implemented at the earliest possible opportunity. Field crews are trained in locating sampling sites by GPS. Stations that are not accessible by helicopter due to safety concerns or potential damage to the aircraft will not be sampled and will be replaced by oversample stations as described in Appendix 3.

All field crews will have cell phones and satellite phones. Should problems arise in the field, they will have direct communication ability with the Project Manager and support personnel in the laboratory at all times.

## **B2.4** Sampling Equipment, Preservation and Holding Time Requirements

Sampling equipment, preservation and holding time requirements for the study parameters are addressed in the SESD SOPs and SERP SOPs.

Sample container selection and preparation have been overseen by the project Laboratory QA Officer. Container types and volumes are identified in Table 3.

Sample preservation methods will be overseen by the project Laboratory QA Officer and are identified in Table 3.

Field equipment includes properly calibrated YSI model 6920 water quality sondes, Garmin GPS units, Trimble GPS units, and digital cameras (Nikon Coolpix 520).

Equipment needs are identified in the project load out checklist.

## B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Sample handling and shipping requirements are found in the SESD Sample Evidence and Management SOP and the Packing, Marking, Labeling and of Environmental and Waste Samples SOP (see Table1). Samples to be analyzed by the SESD ASB laboratory will be shipped via overnight courier under proper chain-of-custody to the laboratory facility located in Athens, GA. The samples to be analyzed by the FIU Laboratory will be transferred by hand on the sampling date, also under proper chain-of-custody. Chain-of-custody tracking and management for the project is performed using EPA's SCRIBE software.

These procedures ensure that:

- samples are collected, transferred, stored and analyzed by authorized personnel,
- sample integrity is maintained during all phases of sample handling and analyses, and
- an accurate written record is maintained of sample handling and treatment from the time of collection through laboratory procedures to disposal.

A sample is in custody if it is in actual physical possession or it is in a secured area that is restricted to authorized personnel. Custody for this project is primarily concerned with the tracking of sample collection, handling and analysis.

Samples will be numbered using the format X1X2-YYY-AAB, where X1 is the sampling event (W = wet season) and X2 is the replicate designation (A, B, or C). YYY is the sampling site designation and AA indicates sample media. The sample media codes are as follows:

SW - surface water

PB - periphyton, benthic mat (not floating)

BW - bottom water

PC - periphyton collected from the water column

FS - fish

SD - sediment

FC - floc

SG - sawgrass

The final character "B" is the laboratory designation, as follows:

S - SESD,

FC - FIU mercury lab,

FN - FIU nutrient lab

FW - FIU biogeochemistry lab

#### **B4 ANALYTICAL METHODS**

The project analytes are provided in Tables 2 and 3. Details of the analytical methods and equipment required for each of the methods are addressed in the SESD and SERC QA Plans. These references include, if applicable, any sub-sampling and/or extraction/preparation methods, laboratory decontamination procedures and materials, and waste disposal requirements. The analytical laboratories will follow their respective approved SOPs which are based on EPA methods and published methods.

Analytical laboratory turnaround time is 60 days.

## **B5 QUALITY CONTROL REQUIREMENTS**

QC requirements are discussed as part of the validation section (Section D). Field quality control measures will be in accordance with the SESD Operating Procedure for Field Sampling Quality Control (Table 1). For example, method blanks, including field bottle blanks, field equipment blanks, and trip blanks, will be used. Before the survey, rinse blanks will be performed on all gloves for trace-level mercury, at the rate of one per lot. Rinse blanks will be

performed on all sample containers before the survey, at the rate of one per lot. Blank samples will be analyzed for the constituents intended for a given container during the survey. Emphasis will be placed on the three critical pollutants, mercury, phosphorus and sulfur. Containers to be blanked include all of the various bottles, syringes, zip-lock bags and buckets used to hold the media sampled. Filters and screens will also be blanked. Trip blanks will be done for mercury, one per helicopter per day. Equipment rinse blanks for mercury will be collected from the vacuum chambers nightly by EPA or ESAT.

## B6 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE REQUIREMENTS

#### B6.1 Purpose/Background

Equipment testing, inspection and maintenance procedures are addressed in the SESD SOPs (Table 1) and SERC QA Plans. The purpose of this testing is to ensure that all instruments and equipment are maintained in sound operating condition and are capable of operating at acceptable performance levels.

#### **B6.2** Testing, Inspection, Maintenance

Field measurement of in-situ water quality parameters (conductivity, pH, dissolved oxygen, temperature, turbidity) will be performed with a YSI model 6920 sonde. These instruments will be inspected and calibrated daily before sampling and end checked to determine if they are operating within acceptable ranges. Instrument sensitivities are presented in Table 4. Instruments will be calibrated and checked according SESD operating procedure and manufacturers specifications.

## **B7 INSTRUMENT CALIBRATION AND FREQUENCY**

#### B7.1 Purpose/Background

Calibration refers to checking instrument measurements against standards with known valid relationships to nationally recognized performance standards.

#### B7.2 Instrumentation Requiring Calibration

Field and laboratory equipment associated with this project that are calibrated are listed in the laboratory QA Plans.

#### **B7.3 Calibration Methods**

All field and laboratory instruments are calibrated and checked for proper function prior to all analyses. Documentation of calibration for analytical instruments will be maintained by each laboratory and by SESD for field instruments. Proper working condition of the YSI sonde will be verified with newly purchased standard buffer solution (pH), standard solutions (conductivity and turbidity), and water-saturated air (dissolved oxygen) as per the manufacturer's instructions and SESD SOPs.

Calibration procedures for laboratory equipment are included in the individual laboratory SOPs.

#### **B7.4 Calibration Apparatus**

This section is not applicable. All instruments are calibrated using standard materials.

#### **B7.5** Calibration Standards

Primary standards are purchased from reliable scientific supply firms. The standards received by the Project Laboratories and Field Team will be inspected, dated, initialed and stored in the appropriate storage area for that standard (e.g., desiccator, refrigerator or freezer). Once opened, the standards will be dated and initialed again. The manufacturer's certificates for standards received will be kept on file at the Project Laboratories.

#### **B7.6 Calibration Frequency**

Frequency of calibration of field instruments is provided in the appropriate SOP. Calibration of laboratory instruments generally occurs prior to or during each use. After instrument calibration, an initial calibration verification sample is run at the start of each analytical batch (a batch equals approximately 20 samples), and continuing calibration verification checks are run after approximately every 10 samples and/or the end of the batch.

#### **B8. SUPPLIES AND CONSUMABLES**

The purpose of this element is to document that a system for receiving, inspecting and accepting supplies and consumables that may directly or indirectly affect the quality of the project or task is in place in the analytical laboratories. The on-site performance evaluation audit

(Section D) will include inspection of laboratory protocols and documentation for proper receipt, inspection, cleaning, labeling, decontamination, etc. of supplies and consumables as necessary.

The project Field QA Officer is responsible for purchasing of supplies and consumables. Purchase decisions are coordinated with the project Laboratory QA Officer and are coordinated with the various analytical labs. All containers, reagents and preservatives will conform to requirements specified in the appropriate SOPs. All buffers and standards will be checked for expiration dates and appearance.

Glass bottles used for trace level mercury analyses will be cleaned in the SESD lab and tested for mercury content prior to use.

## B9. DATA ACQUISITION REQUIREMENTS (NONDIRECT MEASUREMENTS)

No non-direct measurements are anticipated.

#### B10. DATA MANAGEMENT

#### B10.1 Purpose/Background

This element is an overview of operations and analyses performed on raw ("ascollected") data to change their form of expression, location, quantity or dimensionality. These operations include data recording, validation, transformation, transmittal, reduction, analysis, management, storage and retrieval. Selected field measurements and analytical results and associated information will be transferred to electronic files. These files can be created in any spreadsheet program that is compatible with Microsoft Excel.

### B10.2 Data Recording and Reduction

Data recording shall be accomplished using established techniques. The calculations required to complete the reduction of data may be performed manually or with the aid of automated data processing systems. In either case, the SOPs for the testing/analysis of samples will specify the calculations and the mode for raw data processing. To reduce the potential for errors in data transcription, the manual transfer of data will be minimized. All calculations performed manually will be checked for accuracy by someone other than the person performing the original calculation. Checking shall be documented by signature and date in the raw data. Separate documentation is acceptable, provided traceable records are maintained. For automated

data processing or recording, the accuracy of values will be verified through the use of standards or raw data inputs with known results.

#### **B10.3 Data Transformation**

Data analysis results will be provided in a comprehensive report that will be prepared following field and laboratory tasks. Since all laboratory data will undergo data validation, it will be necessary for the laboratories to produce and provide a data deliverable sufficient to perform data validation. As a result, the elements provided in Section D1 below must be included in the final laboratory report.

#### **B10.4** Data Transmittal

Field data will be entered into electronic files in either Microsoft Excel or Access by EPA personnel or contractors. Lab instruments produce electronic files, which will be sent electronically to the laboratory QA/QC Project Officer . Laboratory data files will be formatted according to the EPA Region 4 Electronic Data Deliverable (EDD) requirements.

#### **B10.5 Data Analysis**

Summary statistics will be calculated and compared for a number of regional groupings. Analytical results will also be used to create spatial isoconcentration maps (kriging, using Surfer software). Additional statistical analyses of analytical results will likely include cumulative distributions, ANOVAs, regressions, trend analyses and various nonparametric approaches if data are not normally distributed. These analyses will use the data for the entire study area grouped together, or split by geographic regions. Most of these statistical analyses will be performed using, Statistica, PC-SAS, or Excel with the Analyse-it add-in. Excel will be used to develop the cumulative distributions.

#### B10.6 Data Storage and Retrieval

Data received from the field data collectors and the laboratories will be imported into archival files that will not be modified. These files will serve as storage for these data. Any data files needed for data analyses will be created using data extracted from these storage files. For the duration of this project, these files will be stored by the Project Manager, and then managed according to the SESD Control of Records SOP.

#### SECTION C. ASSESSMENT/OVERSIGHT

#### C1. ASSESSMENTS AND RESPONSE ACTIONS

#### C1.1 Purpose/Background

This element of the QAPP describes the internal and external assessments necessary to ensure that:

- all elements of the QAPP are correctly implemented as prescribed,
- the quality of the data generated by implementation of the QAPP is adequate, and
- corrective actions, when needed, are implemented in a timely manner and their effectiveness is confirmed.

Planned external assessments are described in the QAPP, although the most important part of this element is documenting all of these assessments. Generally, internal assessments are initiated or performed by the Laboratory QA/QC Project Officers, Project Managers and/or the field QA/QC Project Officer.

#### C1.2 Assessment of Project Activities

The following assessments are planned as part of the overall QA/QC associated with the project:

Technical Systems Audit (TSA): A TSA is an on-site qualitative audit, where facilities, equipment, personnel, training, procedures and record keeping are examined for conformance to the QAPP. The project will adhere to the SESD Field Branches QMP (Table 1). Laboratory TSAs were conducted during the project planning (May 2013 for FIU and August 2013 for SESD ASB), and another TSA will be conducted in September during laboratory analysis of project samples. There is no room on the helicopters for field auditors. Audits of on-station activities will be accomplished by reviewing 100 % of the field data sheets, data-sonde logging files, GPS logging files, and photographs, from each station. These reviews will be conducted on site at the staging laboratories on the FIU campus. Reviews will take place the same day in the case of the field data sheets, and the following day in the case of the other information to allow time for uploading of files. These reviews will be performed by a designated Field Quality Assurance Officer, not the on-site Project Manager. Corrective action will be taken immediately

regarding deficiencies on the field data sheets. Other deficiencies will be addressed with the crews in the laboratory on the next day.

<u>Data Quality Assessment (DQA)</u>: A DQA will be performed to ensure data collected during the project meet the assumptions under which the DQOs and data collection design were developed, and whether the total error in the data is tolerable. This will be performed by the Field and Laboratory Project Officers.

Performance Evaluation (PE). Use of "blind" PE samples will indicate accuracy and precision of the measurement system. During sampling events the FIU nutrient lab will receive blind PE samples for total phosphorus in water, and the FIU mercury lab will receive blind PE samples for total mercury in water. Historical PE data from the analytical laboratories will also be evaluated. Successful accomplishment of PEs will be based on criteria presented in Section D.

The Laboratory QA/QC Project Officer will perform the TSAs during the project. Results of audits and other assessments that reveal findings of practices or procedures that do not conform to the written QAPP will be reported to the Project Manager in writing within 1 week of the audit. The written summary will provide recommendations for corrective actions. Upon approval of the corrective actions by SESD Management, the field sampling group or analytical laboratory that is the subject of the recommendations will be notified of the finding and the required corrective actions.

#### C2. REPORTS TO MANAGEMENT

Effective communication between all personnel is an integral part of a quality system. Written reports provide a structure for apprising management of the project schedule, the deviations from approved QA and test plans, the impact of these deviations on data quality and the potential uncertainties in decisions based on the data. Verbal communication on deviations from QA plans should be noted in summary form.

Management reports are anticipated on a routine frequency of once per week during sampling and analytical activities associated with the sampling event. The anticipated benefits of these reports include alerting the management of data quality problems, proposing viable solutions and procuring additional resources. If program assessment (including the evaluation of

the technical systems, the measurement of performance and the assessment of data) is not conducted on a continual basis, the integrity of the data generated in the program may not meet the quality requirements. These audit reports, submitted in a timely manner, will provide an opportunity to implement corrective actions when most appropriate.

The reports to management will originate from three groups: (1) the field sampling/activities group, (2) the analytical laboratories, and (3) the data validation/management group. Reports will be directed to Dr. Peter Kalla, the Project Manager.

Contents of the reports will include (1) status of the project each group is associated with, (2) anticipated activities for the next period, (3) problems or delays encountered and associated resolutions, (4) additional needs, and (5) general comments.

The Project Manager (Dr. Peter Kalla) and the Associate Project Manager (Daniel Scheidt) are responsible for the overall Project Report (including spatial statistical analyses and interpretation of project data) due October 2015. Co-Principal Investigators on the project (Drs. Richards (macrophytes), Scinto (wetland geochemistry), and Cai (mercury)) are responsible for scientific reports that interpret data.

Entities expecting the Project Report as a condition of funding or sampling permit approval include EPA WPD, the Miccosukee Tribe of Indians of Florida, National Park Service and U. S. Fish and Wildlife Service.

## SECTION D. DATA VALIDATION

This section presents validation activities that occur before, during, and after the data collection phases of the project. QA/QC sampling, analytical and validation requirements described in this QAPP will generally apply to both the pilot study and the wet season sampling periods during the Phase IV assessment. However, various nonstandard or developmental sampling protocols and analytical methods/protocols utilized during pilot sampling may not be continued in the subsequent wet season sampling phase. These pilot study protocols will be closely evaluated based on a number of criteria including problems encountered, volume and applicability of data collected compared to the sampling effort, cost of data collection, and data needs to address sampling design parameters. Based on this evaluation, sampling parameters and protocols, as well as analytical methods (and to some degree, validation requirements) will be refined as necessary and included in the sampling efforts.

The Southeast Environmental Research Center of Florida International University houses three of the analytical laboratories used by this project. All three labs (mercury, nutrients and soils) have NELAC accreditation. The fourth lab used by the project, the EPA SESD lab, is ISO 17025 accredited. The FIU lab was audited on-site by the Project Laboratory QA Officer in May 2013. Results were communicated to the Project Manager by memorandum. The SESD ASB laboratory was audited in August 2013 by the Project Laboratory QA Officer. All labs have provided SOPs to the Project QA Officer. A laboratory-specific list of analyses for the project is included in Table 2.

Section D1 of this QAPP provides criteria that will be used to review and "validate" (*i.e.*, accept, reject or qualify) data produced during this project by the contract laboratories. The process to be used during validation is discussed in Section D2. Sections D2 and D3 describe how limitations on the use of the data will be reported to the data users.

## D1. VALIDATION CRITERIA

Validation of the data associated with the project will be achieved with development and review (verification) of documentation to show that the required QA/QC procedures are followed. The QA/QC documentation developed during the project will allow evaluation of the following indicators of data quality:

- integrity and stability of the samples,
- instrument performance during analysis,
- sample contamination,
- identification and quantitation of analytes,
- analytical precision, and
- analytical accuracy.

The following sections provide criteria that must be met to evaluate and validate data generated during the project. Specific exceptions (e.g., certain sample and analytical methods) to these validation criteria are discussed in subsections below. In addition, certain corrective actions to resolve QC problems are presented in these following sections.

General QA/QC requirements for the project include the following:

- Field sampling activities will follow SESD's SOPs (Table 1) and the protocols described in the FIU Plan of Study (Appendix 5).
- Analytical laboratories involved with the project have established and implemented comprehensive QA programs to define the reliability of the analytical results produced for this project. The QA programs have been documented in written QA/QC plans that have been approved by SESD OQA.
- Analytical laboratories utilized will comply with the EPA approved laboratory QA/QC plans submitted as required during this project. Any proposed modifications to the laboratory QA plans must be reviewed and approved by EPA prior to implementing the modification.
- Sample containers, blank water, and equipment Field and laboratory personnel will prepare and use containers and equipment that do not contribute contamination to samples detectable as critical constituents. Field equipment blanks will be utilized to verify this requirement by comparing analyte concentrations in the wash water before and after it contacts the equipment. Blank requirements specifically apply to surface water (media) samples only at a level of 1 blank prepared (field or equipment) per batch or for approximately every 20 samples collected.
- Sample custody and tracking Field and laboratory custody will utilize Scribe software and will follow SESD Sample Evidence and Management SOP. Chain-of-custody will be maintained throughout sampling, transport and analysis.
- Performance Evaluation (PE) Sample PE samples will be obtained from certified sources and submitted to the analytical laboratory for evaluation and qualification during data validation. PE samples will be obtained and used for validation for water phosphorus and low level mercury,.

- Documentation Participating laboratories will assure all documents including but not limited to logbooks, chain-of-custody records, sample work sheets, sample run logs, instrument raw data, bench sheets, sample preparation records and data deliverable reports are prepared.
- Sample Data Reports Participating laboratories will complete and submit data summaries (spreadsheets) in both hard copy and electronic copy formats. Laboratory MDLs for each parameter are required with these reports, calculated according to 40 CFR Part 136, Appendix B, or other approved method.
- QC Data Reports Along with sample results from each batch of environmental samples, the participating laboratories will submit results of all field generated QC samples including equipment blanks, field duplicates (co-located samples) and field blanks. Participating laboratories will compile and submit QC data for these sample types. The laboratory will also compile and submit results of laboratory QC samples for replicates and spikes including the parameter and matrix. Relative percent difference (RPD) for duplicates or relative standard deviation (RSD) will be required for precision evaluation utilizing laboratory split samples. Percent recovery (%R) or percent difference (PD) for standard reference materials (SRMs) will be required for accuracy evaluation.
- Data entry The analytical laboratories or EAB personnel will enter data following standard procedures for manual entry. Accuracy of transcription for the data will be checked by another person. Data plots and descriptive statistics will be used to screen accuracy of data entry where historical data exist.

Specific QA/QC criteria for validation and verification of data associated with the project include the following; these analytical data will be available for inspection as necessary:

- Documentation packages for data submittals.
- Narrative description of the data report packages (including range of samples analyzed, analytical methods, sample holding times summary, descriptions of problems encountered, and explanation for any QA/QC samples that do fall outside project acceptance criteria); applicable comments relating to sample integrity or data quality.
- Chain-of-custody documentation and summary (including completed forms that match all data submitted with package).
- Summary of results (including data tables and statement regarding achievement of MDLs specified in the project statement of work - Attachment 1).
- Field and/or laboratory data for 100 percent of analyses of "critical" parameters for the batch (mercury, methyl mercury, sulfate, and phosphorus). Additional complete data packages may be required for the remaining parameters, depending upon ongoing QA evaluations by the Project Laboratory QA Officer during the project. This includes:
  - Sample log-in documentation.

- Manual calculations including raw data, formulae utilized, any conversion constants and an example calculation. Verification of one of each type of calculation will be necessary.
- Instrument printouts, bench sheets, digestion worksheets, sample preparation logs and other sample analysis and preparation documentation/calculations.
- Sample dates and times of collection, digestion and analysis along with sample volumes and digestion volume, and percent solids (as appropriate).
- QC Sample Documentation
  - Instrument calibration documentation An instrument calibration curve will be prepared at minimum at the beginning of each day of analysis utilizing at least three standards plus one blank (five standards and one blank for total mercury and methyl mercury).
  - Laboratory Method Blanks A laboratory method blank will be analyzed at the start of each analytical batch.
  - Internal calibration data (initial and CCV-continuing calibration verification data)
     Documentation of initial calibration and mid-level CCV at the first of each batch and one per 10 samples analyzed. CCV will be prepared from standard reference material from source(s) which attest to the concentration of the standard source.
- QC Sample Data for each batch of 20 samples or fewer, the analytical laboratory will provide data for the following QC samples:
  - One laboratory method blank that will be included with every step in the analytical procedure.
  - o One laboratory replicate.
  - One matrix spike For water, the matrix spike will be designed to result in a sample analysis concentration that does not exceed 2 times the PQL or 2 times the expected sample concentration, whichever is larger. For solids, the matrix spike will be designed to result in a sample analysis concentration that does not exceed 2 times the unspiked sample.
  - O It is anticipated that one PE sample will be analyzed by the appropriate laboratory for low level mercury, phosphorus, and sulfate at a frequency of one per week over the duration of the project. The PE sample must be prepared following the instruction from the provider and analyzed along with field samples following the same procedures as the samples.
  - One SRM for the matrix in an appropriate concentration that will not exceed the concentration of the most concentrated standard.

Data will be available for inspection.

There are no project specific calculations or algorithms.

### D2. VALIDATION METHODS

Validation methods to assess the following general QA/QC requirements for the project are presented in this section. Any nonconformance issues for this section will result in implementation of corrective actions to address the issue, documentation of the corrective action, and a preparation of narrative description to describe potential impacts to data quality due to the problem. SESD management is responsible for approval of any corrective actions implemented during field sampling.

- Sample/data management protocols will be verified by conducting on-site field and laboratory PE audits.
- QA program and written QA plan preparation and acceptance will be validated during pre-sampling review by EPA Region 4 SESD OQA.
- Compliance with the EPA approved laboratory QA plans will be validated by (1)
  performing an on-site laboratory audit during the wet season sampling/analysis activities
  and (2) on-going review of data deliverable packages submitted with analytical results
  packages. Verification of supporting functions such as sample custody, reagent and
  standards preparation, sample preparation, equipment and container cleaning, and
  calibration will also be performed via on-site PE audit of the analytical laboratory.
- Appropriateness of sample containers, blank water and equipment will be validated by
  analysis of blanks (field and equipment) during the project as well as review of laboratory
  operations during a PE audit described above. Successful performance for blank usage
  and analysis is defined as no differences (<3 times the MDL) in analytical results
  between blanks and source water utilized for preparation of blanks.</li>
- Sample custody and tracking conformance will be validated by review of documentation submitted with data report packages as well as by direct observance during a PE audit described above. Conformance to this requirement will be met with custody documented for all samples. Non-conformance may result in limiting the usability of the data.
- Preparation and storage of appropriate project documentation will be validated by means
  of reviewing data deliverable report packages and on-site PE audits.
- Completeness and accuracy of reports will be validated by reviewing and verifying data entry QA/QC results and during data analysis and outlier identification.

Specific QA/QC targets and validation methods of data associated with the project include:

 Documentation packages for data submittals will be validated by verifying necessary components included with each package submitted to EPA personnel. Approximately

10% of the test results for critical parameters for each analytical batch, parameter group and matrix, will be recalculated, as applicable.

## QC Sample Documentation

- Instrument calibration documentation A correlation coefficient of 0.995 or better using least squares fit unless the approved calibration method permits verification of the initial calibration using fewer standards. Documentation of low- and midrange CCV checks at the first of and during analyses will be required as well as one SRM. The laboratories will maintain this documentation.
- Laboratory Method Blanks If the difference between results from the laboratory method blank and the source water used to prepare the blank exceeds the action limit of >3 times the MDL, documentation of corrective actions taken to reduce it to below the action limit prior to any analysis is required. Documentation of such corrective actions will be prepared and maintained at each Project Laboratory.
- O Internal calibration data (continuing calibration verification data) If results differ by >15% (as defined by the Method) from the known value or the initial check, whichever is appropriate, the laboratory will take corrective action(s) to reduce the difference to below 15% and document the problem and action(s) taken. Any samples analyzed after the last passing CCV and prior to the failing CCV will be reanalyzed after corrective action(s) are taken and a passing CCV is analyzed.

### QC Samples

- Laboratory Method Blank The difference between blank results and source water must be <3 times the MDL. Action to determine the cause of the contaminant, correct the problem, and document such actions must be taken and documented when results are >3 times the MDL.
- Equipment (Field) Blank Differences between blank results and the source water
   3 times the MDL will result in the samples collected with the field equipment used to produce the blank on the same day of sampling to be qualified to alert data users to potential cleaning or sampling problems.
- Replicated Samples Where samples are "split" in the field, RPD should be
   20%. Field split samples with RPDs >20% will be qualified to alert data users to potential sampling problems. These criteria apply to analytes >5 times the MDL.
- Laboratory Standards and CCV Percent difference from initial calibration check should be <15%.</li>
- Matrix Spikes Percent recovery for matrix spikes should fall within the range of 75 to 125%, or as defined in the laboratory method SOP, of the spiked concentration for all media. However, matrix spike recovery outside this range will not by itself result in a "reject" qualifier. Rather, the data will be qualified as having a matrix effect to alert data users.

 SRMs, Blank Spikes, PE Samples - Accuracy as percent recovery and precision of replicates as RPD or RSD for those samples must meet Project DQO requirements (Appendix 1).

All reported data will be validated according to Section D of this QAPP. When reporting data to EPA, the following data qualifiers are anticipated for use with this project:

- $\underline{U}$  Analyte not detected at or above the MDL.
- <u>J</u>- Concentration reported should be considered an estimate. The data are acceptable for use as determined by specific data users but certain QC criteria were not met. For example:
  - data were above or below the appropriate linear calibration range,
  - holding times were exceeded,
  - certain QC documentation was not prepared as required, or
  - the analyte was detected below the MDL.
- A- Analyte was analyzed as a replicate and the value reprinted is the mean of the replicates.
- $\underline{R}$  Batch QC data did not meet DQO required accuracy/precision criteria required to allow use as stated.
- $\underline{M}$  Analyte exhibits potential matrix effect based on matrix spike recovery outside of 75 to 125% range. Data are usable.
- $\underline{\mathbf{D}}$  Analyte concentration reported as the result of a secondary dilution. Discrepancies between two runs may be due to dilution errors. Data are usable provided other criteria are met.
- $\underline{B}$  Analyte concentration in the associated blank was >3 times the MDL.

# D3 RECONCILIATION WITH DATA QUALITY OBJECTIVES

The purpose of element D3 is to outline and specify, if possible, the acceptable methods for evaluating the results obtained from the project. This element includes scientific and statistical evaluations of data to determine if the data are of the right type, quantity, and quality to support their intended use.

## D3.1 Reconciling Results with DQOs

There will be two phases of reconciliation of the results with the DQOs. In Phase A, statistical analyses will be performed to compare computed estimates (*e.g.*, recovery, precision, PE sample variance) with DQOs specified in this QAPP. This information will be provided to the Project Manager and QA/QC Laboratory Officer. In Phase B, the user will determine if the data results meet their needs and objectives. Phase B supersedes any and all Phase A QA/QC analyses and results, because the purpose of any QA/QC program is to provide information of known quality so that the user can determine if the data meet their needs and objectives.

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Figure 2a. Aerial Photo of September 2013 sampling stations.

Everglades Phase IV REMAP

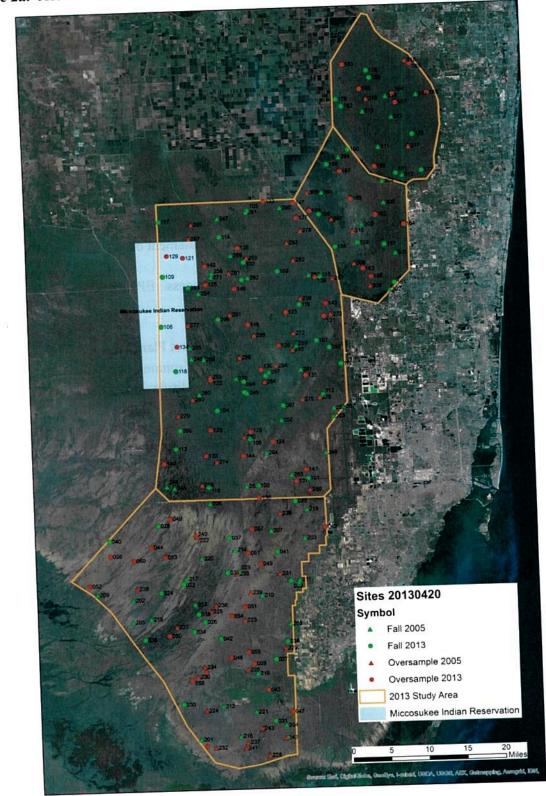


Figure 2b. Map of September 2013 sampling stations.

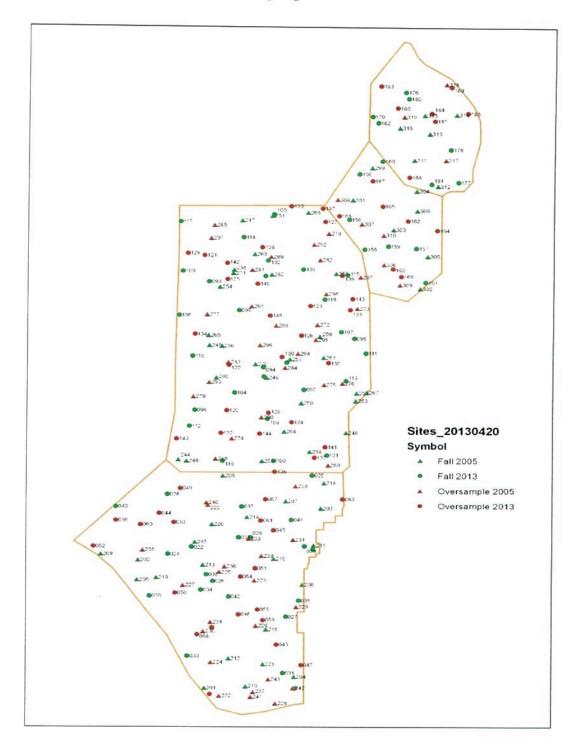


Table 1. List of Policies and Standard Operating Procedures (SOPs) by Institution.

EPA Policies, Plans and SOP's		
(available at http://www.epa.gov/region4/sesd/fbqstp/inc		
Policy Name	Number	Revision
Field Branches Quality Policy	SESDPLCY-001	R4
Plan Name	Number	Revision
SESD Field Branches Quality Management Plan	SESDPLAN-001	R5
Quality System Procedure Name	Number	Revision
Document Control	SESDPROC-001	R6
Control of Records	SESDPROC-002	R5
Report Preparation and Distribution	SESDPROC-003	R4
Sample and Evidence Management	SESDPROC-005	R2
Competency and Proficiency Testing	SESDPROC-006	R3
Training	SESDPROC-007	R4
Logbooks	SESDPROC-010	R5
Field Sampling Quality Control	SESDPROC-011	R4
Field Measurement Uncertainty	SESDPROC-014	R1
Purchasing of Services and Supplies	SESDPROC-015	R4
Project Planning	SESDPROC-016	R2
Equipment Inventory and Management	SESDPROC-108	R4
Field Equipment Center Management	SESDPROC-900	R0
Field Measurement of Dissolved Oxygen	SESDPROC-106	R2
Field pH Measurement	SESDPROC-100	R3
	SESDPROC-101	R5
Field Specific Conductance Measurement	SESDPROC-102	R3
Field Temperature Measurement	SESDPROC-102	R3
Field Turbidity Measurement	SESDPROC-103	R3
Global Positioning System		3500507
In-Situ Water Quality Monitoring	SESDPROC-111	R3
Sediment Sampling	SESDPROC-200	R2
Surface Water Sampling	SESDPROC-201	R3
Packing, Marking, Labeling and Shipping of Environmental and Waste Samples	SESDPROC-209	R2
Fish Field Sampling	SESDPROC-512	R3
Florida International University SO	Ps	
Procedure Name	Number	Version Date
Sample Receipt and Data Reporting	010-04	9/16/05
Determination of Chlorophyll-a in Water Samples	SERC-003	3/8/10
Determination of Total Nitrogen in Water	SERC-006	3/5/12
Determination of Total Phosphorus in Water, Sediments, Tissue and Soil Samples	SERC-008	3/15/12
Determination of Filtered Nutrients in Water Samples (N+N, NO2, NH4, SRP)	SERC-004	7/20/08
Determination of Total Mercury in Water Samples	001-04	2/6/08
Determination of Total Mercury in Soils and Sediments	002-04	2/6/08
Determination of Total Mercury in Tissue Samples	003-04	2/6/08
Determination of Methylmercury in Water Samples	004-04	2/6/08
Determination of Methylmercury in Soil and Sediment Samples	005-04	2/6/08
Determination of Methylmercury in Tissue Samples	006-04	2/6/08

Table 2. Laboratory analytical methods and minimum detection levels.

Parameter Lab MDL		SERC (FIU)	SESD/ESAT	SESD/ASB	
		SURFACE WATER			
Total Phosphorus	0.6 ug/L	EPA 365.1(modified)			
Total Nitrogen	0.03 mg/L	ASTM D5176			
Ammonium-N	0.8 ug/L	EPA 350.1	122		
(filtered-0.45)				2-27-4229	
Nitrite-N (filtered)	0.3 ug/L	EPA 353.2			
Nitrate-N	0.7 ug/L	EPA 353.2			
(filtered)					
Phosphate	0.6 ug/L	EPA 365.1			
(filtered)					
Dissolved Organic	1.0 mg/L			SM 5310B-	
Carbon (DOC)				2000	
Sulfate	0.02 mg/L			EPA 300.0	
Chloride	0.1 mg/L			EPA 300.0	
Chlorophyll a		SERC SOP 009-98		21.11.500.0	
Total Mercury	0.3 ng/L	EPA 1631E			
Methyl Mercury	0.02 ng/L	EPA draft1630 modified			
		BOTTOM WATER			
Soluble Sulfide	0.01 mg/L	BOTTOM WATER	EPA 8131-		
			modified		
			(HACH)		
	SOI	L, FLOC and PERIPHYTON	(IIIIeII)		
Total Mercury	4.3 ug/kg	EPA 7474 (modified)	1		
Methyl Mercury	0.2 ug/kg	EPA 1630 (modified)			
Total Phosphorus	0.06 mg/kg	EPA 365.1			
Total Nitrogen	0.02 mg/kg	SERC SOP			
Total Carbon	0.35 mg/kg	SERC SOP			
Ash Free Dry	0.02 mg/kg	ASTM D2974-87			
Weight					
Bulk Density	0.001 g/cc	ASTM D4531-86			
THURST TO BE		SOIL and PERIPHYTON			
Mineral Content	3 %	ASTM D 2974-87	T T		
Methane	A 2015 A	ASTM D 2974-87			
Carbon Dioxide		ASTM D 2974-87			
	F	LOC and PERIPHYTON			
Chlorophyll a	1	SERC SOP 009-98			
omorophyn u		SOIL			
Н		SOIL	EDA 150 1		
511		MOCOLUTORIGH	EPA 150.1		
Total Mercury	3.2 ug/kg	MOSQUITOFISH		Julie I I I I I I I I I I I I I I I I I I I	
otal wicicury	3.2 ug/kg	EPA 7474 (modified)			
Fotal Moreum:	4.2 ug/l-c	SAWGRASS			
Total Mercury	4.3 ug/kg	EPA 7474 (modified)			
Methyl Mercury	0.2 ug/kg	EPA 1630 (modified)			
Total Phosphorus	0.06 mg/kg	EPA 365.1			
Total Nitrogen	0.02 mg/kg	SERC SOP			
Total Carbon	0.35 mg/kg	SERC SOP			

Table 3. Media analytes and containers.

Field Container	Color	Filtered?	Analyte	Field Preservation	Ice?	Preserved?	Analytical Lab
			Surface	Water			
250 ml	Clear glass	No	THg, MeHg	Clean, double- bagged, dark	No	No; lab preserved FIU SOP 001-04	FIU - Cai
2x 125 ml poly	Blue tape	No	TP, TN, TC	Store in dark	YES	No; TN lab preserved FIU SOP SERC 006; TP prepared immediately upon lab arrival FIU SOP SERC 008	FIU- Scinto
125 ml poly	Green tape	No	SO4, Cl	-	YES	No	EPA- ASB
60 ml poly	Pink	YES- nylon	NH4, NO3, NO2, PO4	•	YES	No	FIU - Scinto
40 ml VOA glass vial w/acid <sup>2</sup>	Orange	YES- poly sulfone	DOC <sup>2</sup>	Filter via polysulfone, NO HEADSPACE, store in dark	YES	YES; pre- preserved to pH <2 with H <sub>2</sub> SO <sub>4</sub>	EPA- ASB
Filter from chlorophyll a	-	GF/F filter	Chlorophyll a	Folded, in acetone in ampule, dark, on ice	YES	(acetone)	FIU – Scinto
			Botton	n Water		- I I I I I I I	
60 ml syringe, w/Zn acetate	Lavender	No	H2S	No air	No	YES	EPA - ESAT at FIU
			S	Soil			
Plastic bucket- composite of 3 cores 0-10 cm	White	-	THg, MeHg, AFDW, BD, C, N, P, MC, CO2, CH4	-	No	No	FIU- Scinto, Cai
				loc			
Storemore(s) or white bucket	-	-	THg, MeHg, AFDW, BD, C, N, P, CH4, CO2, Chla	-	No	No	FIU – Scinto, Cai
		W- Target	Peri	phyton			
2x Plastic cups, blue lid, white lid		-	THg, MeHg, C, N, P, Chla	-	No	No	FIU – Cai, Scinto
	Wind the Park			Fish	O.		112
Plastic bag with water 4" x 6"	-	-	THg	-	Yes	No	FIU - Cai
To the second				Macrophyte			
Plastic Bag 6" x 10"	Clear	NO	THg ,MeHg	Plastic Bag	No	No	FIU – Cai

Samples will not be placed on ice in the field due to space and weight limitations in the helicopter. Samples will be refrigerated upon receipt in the laboratory.

<sup>&</sup>lt;sup>2</sup> For DOC, three vials are needed at 5% of the stations for laboratory QC.

Table 4. In Situ Equipment Accuracy

Parameter	Units	Measurement Technology	Sensitivity of Primary
Dissolved Oxygen	mg/L	Luminescent Dissolved	Equipment ± 0.1 mg/L
Temperature	°C	Oxygen Probe	± 1% reading
pH	SU	Thermistor	±0.3 °C
Conductivity		Glass electrode	± 0.2 SU
Turbidity	μS/cm	Nickel electrode cell	± 0.5% of reading
- arounty	NTU	Optical probe	Greater of:
Barometric Pressure	hPa		±10% or 2 NTU
· coourc	m a	Pressure sensor	0.80%

Table 5. List of Sample Stations and Oversample Stations

able 5. List of Sample Stations and Oversample Stations  Stratum							
Γ	Station ID	Long	Lat	Type	Region	ENP_2013	
1	R4E13-1022			Fall 2013	ENP	ENP_2013	
100		-80.557949	25.595114	Fall 2013	ENP	ENP_2013	
	R4E13-1024		25.585439	Fall 2013	ENP	ENP_2013	
4		-80.559560	25.755119	Fall 2013	ENP	The state of the s	
5	R4E13-1026		25.527507	Fall 2013	ENP	ENP_2013	
6	R4E13-1027	-80.612721	25.451504	Fall 2013	ENP	ENP_2013	
7	R4E13-1028		25.714442	Fall 2013	ENP	ENP_2013	
8	R4E13-1029		25.621468	Fall 2013	ENP	ENP_2013	
9	R4E13-1030	-80.811878	25.369200	Fall 2013	ENP	ENP_2013	
10	R4E13-1031	-80.618417	25.332457	Fall 2013	ENP	ENP_2013	
11	R4E13-1032	-80.594138	25.299470	Fall 2013	ENP	ENP_2013	
12	R4E13-1033	-80.708703	25.621276	Fall 2013	ENP	ENP_2013	
months of	R4E13-1034	-80.784592	25.509038	Fall 2013	ENP	ENP_2013	
13	R4E13-1035	-80.586406	25.485846	Fall 2013	ENP	ENP_2013	
14	R4E13-1036		25.495985	Fall 2013	ENP	ENP_2013	
15	R4E13-1037		25.687739	Fall 2013	ENP	ENP_2013	
16	R4E13-1038		25.542361	Fall 2013	ENP	ENP_2013	
17	R4E13-1039			Fall 2013	ENP	ENP_2013	
18	R4E13-1040		25.687200	Fall 2013	ENP	ENP_2013	
19	R4E13-1040	-80.601629	25.658982	Fall 2013	ENP	ENP_2013	
20	R4E13-1041			Fall 2013	ENP	ENP_2013	
21	R4E13-1042			OverSamp	ENP	ENP_2013	
22				OverSamp		ENP_2013	
23	R4E13-1044		25.636860			ENP_2013	
24	R4E13-1045					ENP_2013	
25	R4E13-1046					ENP_2013	
26	R4E13-1047			and the second s		ENP_2013	
27	R4E13-1048				Control of the Contro	ENP_2013	
28	R4E13-1049					ENP_2013	
29	R4E13-1050					ENP_2013	
30						ENP_2013	
31	R4E13-1052	2 -81.00085	25.001932			ENP 2013	
32			7 25.537382	OverSam	(1907)	ENP 2013	
33						ENP_2013	
34						ENP_2013	
35						ENP_2013	
36						ENP_2013	
37						ENP_2013	
38			200			ENP 2013	
39	Security Control of the Control of t					ENP_2013	
4				_		ENP 2013	
4						ENP 2013	
4			Annual Control of the				
4							
	4 R4E13-109						
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4	7 R4E13-109	96 -80.79875	6 25.89654	/ Fall 201	3 TANCHO	7,0,0,1_20.0	

9/19/2013 SESD Project ID: 13-0513

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61	R4E13-1110					
62						
63	R4E13-1112					
64	R4E13-1113				WCA3A	11011011_2010
65	R4E13-1114				WCA3A	
66	R4E13-1115				WCA3A	WCA3A_2013
67	R4E13-1116				WCA3A	WCA3A_2013
68	R4E13-1117				WCA3A	WCA3A_2013
69	R4E13-1118				WCA3A	WCA3A_2013
70	R4E13-1119		26.131340	Fall 2013	WCA3A	WCA3A_2013
71	R4E13-1120	-80.733748	25.895892	Fall 2013	WCA3A	WCA3A_2013
72	R4E13-1121	-80.780079	26.227202	OverSamp		WCA3A_2013
73	R4E13-1122		25.991804	OverSamp		WCA3A_2013
74	R4E13-1123		26.117248	OverSamp		WCA3A_2013
75	R4E13-1124	-80.601697	25.870383	OverSamp		WCA3A_2013
76	R4E13-1125		26.174780	OverSamp		WCA3A_2013
77	R4E13-1126		26.053692	OverSamp		WCA3A_2013
78	R4E13-1127		26.298334	OverSamp		WCA3A_2013
79	The second secon	-80.648859		OverSamp	WCA3A	WCA3A_2013
80	R4E13-1129	-80.814322	26.231696	OverSamp	WCASA	WCA3A_2013
81	R4E13-1130		26.008518	OverSamp		WCA3A_2013
82			26.108102	OverSamp		WCA3A_2013
83			25.846857	OverSamp		WCA3A_2013
84	R4E13-1133		26.331994	OverSamp		WCA3A_2013
85	R4E13-1134			OverSamp		WCA3A_2013
86	R4E13-1135			OverSamp		WCA3A_2013
87				OverSamp		WCA3A_2013
88				OverSamp		WCA3A_2013
89				OverSamp		WCA3A_2013 WCA3A_2013
90				OverSamp		WCA3A_2013 WCA3A_2013
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94					WCA3A	WCA3A_2013
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8	TVIL TO THE		26.327229	OverSamp	WCA3A	WCA3A_2013 WCA2A_2013
99	R4E13-1155	-80.454033	26.239806	Fall 2013	WCA2A	WCA2A_2013 WCA2A_2013
00	R4E13-1156	-80.464851	26.400217	Fall 2013	WCA2A	WCA2A_2013 WCA2A_2013
01	R4E13-1157	-80.348831	26.241829	Fall 2013	WCA2A	
02	R4E13-1158	-80.485997	26.303264	Fall 2013	WCA2A	WCA2A_2013
03	R4E13-1159	-80.406352	26.246430	Fall 2013	WCA2A	WCA2A_2013
04	R4E13-1160	-80.418345	26.427390	Fall 2013	WCA2A	WCA2A_2013
05	R4E13-1161	-80.330210	26.167675	Fall 2013	WCA2A	WCA2A_2013
06	R4E13-1162	-80.366030	26.300089	OverSamp	WCA2A	WCA2A_2013
07	R4E13-1163	-80.396512	26.197224	OverSamp	WCA2A	WCA2A_2013
08	R4E13-1164	-80.306253	26.279875	OverSamp	WCA2A	WCA2A_2013
09	R4E13-1165	-80.417536	26.331931	OverSamp	WCA2A	WCA2A_2013
10	R4E13-1166	-80.379546	26.180838	OverSamp		WCA2A_2013
11	R4E13-1167	-80.438406	26.385866	OverSamp		WCA2A_2013
12	R4E13-1168	-80.506081	26.311016	OverSamp	WCA2A	WCA2A_2013
13	R4E13-1176	-80.371315	26.574799	Fall 2013	LOX	LOX_2013
114	R4E13-1177	-80.263896	THE RESERVE OF THE PARTY OF THE	Fall 2013	LOX	LOX_2013
115	R4E13-1178	-80.279409		Fall 2013	LOX	LOX_2013
116	R4E13-1179	-80.439223		Fall 2013	LOX	LOX_2013
117	R4E13-1180	-80.365570		Fall 2013	LOX	LOX_2013
118	R4E13-1181	-80.318627		Fall 2013	LOX	LOX_2013
119	R4E13-1182				LOX	LOX_2013
120					LOX	LOX_2013
121						LOX_2013
122					78 8948000	LOX_2013
123						LOX_2013
124						LOX_2013
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125						LOX_2013
126			25.300752		ENP	ENP SampFall_2005
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128						ENP_SampFall_2005
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14	3 R4E13-121	7 -80.79698	9 25.61155	T Fall 2013	LINI	Litt _Campi an_1000

	Station ID	Long	Lat	Type	Danie	
1.	44 R4E13-121		1 25.738697	Type	Region	
1.	45 R4E13-121	9 -80.874483				ENP_SampFall_2005
1.	46 R4E13-122					ENP_SampFall_2005
14	7 R4E13-122					ENP_SampFall_2005
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15				OverSamp		ENP_SampFall_2005
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15				OverSamp		ENP_SampFall_2005
15				OverSamp		ENP_SampFall_2005
158				OverSamp		ENP_SampFall_2005
159				OverSamp		ENP_SampFall_2005
160			25.618761	OverSamp		ENP_SampFall_2005
161			25.440444	OverSamp		ENP_SampFall_2005
162	112101200		25.594705	OverSamp		ENP_SampFall_2005
163			25.559168	OverSamp		ENP_SampFall_2005
164			25.292272	OverSamp		ENP_SampFall_2005
165		-80.593105	25.731938	OverSamp		ENP_SampFall_2005
166		-80.661997	25.581779	OverSamp	ENP	ENP_SampFall_2005
167		-80.773934	25.696755	OverSamp	ENP	ENP_SampFall_2005
168	R4E13-1241	-80.683629	25.281709	OverSamp	ENP	ENP_SampFall_2005
169	R4E13-1243	-80.597824	25.300095	OverSamp	ENP	ENP_SampFall_2005
170	R4E13-1243	-80.647743	25.319351	OverSamp	ENP	ENP_SampFall_2005
171	R4E13-1244	-80.831421	25.789500	Fall 2013	WCA3A	WCA3A_SampFall_2005
172		-80.769551	26.033048	Fall 2013	WCA3A	WCA3A_SampFall_2005
173	R4E13-1246	-80.653253	25.965218	Fall 2013	WCA3A	WCA3A_SampFall_2005
174	R4E13-1247	-80.703995	26.301314	Fall 2013	WCA3A	WCA3A_SampFall_2005
175	R4E13-1248	-80.490576	25.847231	Fall 2013	WCA3A	WCA3A_SampFall_2005
	R4E13-1249	-80.815010	25.786471	Fall 2013	WCA3A	WCA3A_SampFall_2005
176	R4E13-1250	-80.582287	25.911661	Fall 2013	WCA3A	WCA3A_SampFall_2005
177	R4E13-1251	-80.642605		Fall 2013	WCA3A	WCA3A_SampFall_2005
178	R4E13-1252	-80.469804		Fall 2013	WCA3A	WCA3A_SampFall_2005
179	R4E13-1253		25.786277	Fall 2013	WCA3A	WCA3A_SampFall_2005
180	R4E13-1254		26.158335	Fall 2013	WCA3A	WCA3A_SampFall_2005
181			26.187276	Fall 2013	WCA3A	WCA3A_SampFall_2005
182	R4E13-1256				WCA3A	WCA3A_SampFall_2005
183	R4E13-1257				WCA3A	WCA3A_SampFall_2005
184	R4E13-1258			Fall 2013	WCA3A	WCA3A_SampFall_2005
185					WCA3A	WCA3A_SampFall_2005
186			25.964751		WCA3A	WCA3A_SampFall_2005
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	Station ID	Long	Lat	Туре	Region	WCA3A_SampFall_2005
192	R4E13-1266					
193	R4E13-1267					WCA3A_SampFall_2005
194	R4E13-1268	-80.564739	25.806149	Fall 2013		WCA3A_SampFall_2005
195	R4E13-1269	-80.678095	26.229370	Fall 2013	WCA3A	WCA3A_SampFall_2005
196	R4E13-1270	-80.675900	25.993610	Fall 2013	WCA3A	WCA3A_SampFall_2005
197	R4E13-1271		26.188227	Fall 2013	WCA3A	WCA3A_SampFall_2005
198	R4E13-1272	-80.550006	26.076830	OverSamp	WCA3A	WCA3A_SampFall_2005
199	R4E13-1273	-80.468924	26.111115	OverSamp	WCA3A	WCA3A_SampFall_2005
200	R4E13-1274	-80.723323	25.834822	OverSamp	WCA3A	WCA3A_SampFall_2005
201	R4E13-1275	-80.535783	25.949691	OverSamp	WCA3A	WCA3A_SampFall_2005
202	R4E13-1276	-80.498619	25.952711	OverSamp	WCA3A	WCA3A_SampFall_2005
203	R4E13-1277	-80.774528	26.098256	OverSamp	WCA3A	WCA3A_SampFall_2005
204	R4E13-1278	-80.527332	26.273462	OverSamp	WCA3A	WCA3A_SampFall_2005
205	R4E13-1279	-80.801760	25.924705	OverSamp	WCA3A	WCA3A_SampFall_2005
206	R4E13-1280	-80.527030	25.776751	OverSamp	WCA3A	WCA3A_SampFall_2005
207	R4E13-1281	-80.683098	26.195541	OverSamp	WCA3A	WCA3A_SampFall_2005
208	R4E13-1282	-80.544532	26.216878	OverSamp	WCA3A	WCA3A_SampFall_2005
209	R4E13-1283	-80.730638	25.997594	OverSamp	WCA3A	WCA3A_SampFall_2005
210	R4E13-1284	-80.615306	25.985760	OverSamp		WCA3A_SampFall_2005
	R4E13-1285	-80.760665	26.290992	OverSamp		WCA3A_SampFall_2005
211	R4E13-1286	-80.634118	26.075003	OverSamp		WCA3A_SampFall_2005
212	R4E13-1287	-80.462535	26.179477	OverSamp		WCA3A_SampFall_2005
213	R4E13-1288	-80.756094	25.791152	OverSamp		WCA3A_SampFall_2005
214	R4E13-1289	-80.644795		OverSamp		WCA3A_SampFall_2005
215	R4E13-1209	-80.662767	25.881391	OverSamp		WCA3A_SampFall_2005
216	R4E13-1290	-80.683984		OverSamp		WCA3A_SampFall_2005
217				OverSamp		WCA3A_SampFall_2005
218				OverSamp		WCA3A_SampFall_2005
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40			20 500===	Туре	Region	Stratum
			26.526759	Fall 2013	LOX	LOX_SampFall_2005
12			26.525606	Fall 2013	LOX	LOX_SampFall_2005
	R4E13-1316		26.498530	Fall 2013	LOX	LOX_Samprail_2005
	R4E13-1317	-80.289213	26.420001	OverCarre	1.011	LOX_SampFall_2005
4	R4E13-1318	-80 288577	26.501570	OverSamp		LOX_SampFall_2005
5	R4E13-1319	-80 3744EC	20.591570	OverSamp	LOX	LOX_SampFall_2005
_	11.12.10 1010	-00.374456	26.522116	OverSamp	LOX	LOX_SampFall_2005

# APPENDIX 1: DATA QUALITY OBJECTIVES

9/19/2013 SESD Project ID: 13-0513

# **Everglades REMAP Phase IV Data Quality Objectives**

STEP	DATAQ	UALITY OBJECTIVES	DESCRIPTION
1	State the Problem	Concise description of the problem     Identify members of the planning team and the primary decision maker     Develop a conceptual model of the environmental hazard to be investigated     Determine resources - budget, personnel, and schedule	Mercury contamination, nutrient loading, hydropattern modification, and habitat alteration are impacting the Everglades ecosystem. Environmentally sound, cost-effective restoration of the Everglades ecosystem depends on identifying sources, causes and interactions, along with tracking the effectiveness of control and restoration efforts. Over \$10 billion dollars are estimated to be spent on this restoration effort. About \$1 billion have been spent to date on phosphorus control efforts. Groups interested in data from this project include numerous Phase I - III data users from Federal, State, and local governments, Indian tribes, non-governmental organizations, academia, and the private sector.  The Team: The team consists of the Project Manager, SESD; Associate Project Manager, WPD; Laboratory Quality Assurance Officer, SESD; Field Quality Assurance Officer, SESD; Analytical Laboratory Directors; and the Contract Officer Representative. This team includes individuals with expertise in wetlands ecology, water quality, chemistry, the Everglades, field methods, laboratory analytical methods, quality assurance and quality control, and environmental statistics.  The Primary Decision Maker The primary decision maker for the Project team is the Project Manager. Other decision makers include the Associate Project Manager, and Directors for the Water Protection Division and Science and Ecosystem Support Division.
		• Identify the	Tens of millions of dollars are being spent each year by the federal and state governments on monitoring and assessment to determine the magnitude, extent, trends and causes of the mercury contamination, eutrophication, hydropattern modification and habitat alteration problems. This Project has a budget of \$700K. Approximately 50 field and laboratory staff will be involved. The survey is scheduled for late September through mid-October 2013.  Principal study question:
G	lentify the oal of the tudy	principal study question  Define the alternative actions that could result from resolution of	The principal study questions.  The principal study questions were identified as part of the original 1993 proposal and specification of the DQOs. They can be broadly stated as "What is the magnitude and extent of mercury, phosphorus, and sulfur pollution, and of soil loss, in the Everglades, and is it getting better or worse?"  Alternative actions that could result from resolution of the

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CTED	DATA OHA	LITY OBJECTIVES	DESCRIPTION
2 (cont'd)		For decision problems, develop decision statements(s), organize multiple decisions.	in answering this question were identified during the initial phases of the Project. These logic pathways and alternative action formulations are a major part of the Problem Formulation phase of the Ecological Risk Assessment Framework that forms the foundation of this study. Dichotomous trees were formulated for each of the logic pathways developed during the initial Project phases. These trees were developed prior to the initiation of the field sampling and were used to assist in the formulation of the preliminary project DQOs.  Decision Statements Combining Principal Study Questions and Alternative Actions:  • Decide how the relative ecological risk from mercury contamination compares with the risks from nutrient additions, hydropattern modification, and habitat alteration.  • Determine if controlling these other stressors will eliminate mercury contamination; if not, determine procedures that can be used to eliminate mercury contamination.  • Determine if phosphorus conditions have changed since the 2005 Phase III Project survey.  • Determine if mercury conditions have changed since the 2005 Phase III Project survey.  • Determine if sulfur conditions have changed since the 2005 Phase III Project survey.  Organize multiple decisions.  Multi-decision logical pathways will be refined as the Project proceeds and new information is collected and analyzed.  What needs to be estimated, and key assumptions.  The magnitude and extent of pollution in the Everglades, and change in same between surveys, assuming the probabilistic design is unbiased.
3	Identify Information Inputs	<ul> <li>Identify types &amp; sources information needed to resolve decisions or produce estimates.</li> <li>Identify basis of information that will support choices made in later steps</li> </ul>	Determine sources for each item of information identified.  The Everglades Ecosystem Assessment Program is a key source of information needed by managers to address the
		of the DQO process.  • Select appropriate sampling/analysis methods for generating information	Identify the information that is needed to establish the action level.  The criteria used to establish the action level will be:  a. Variability - ecological effects significantly different from natural variability.

STEP	DATA QU	ALITY OBJECTIVES	DESCRIPTION
			<ul> <li>b. Endpoints – mercury toxicity, cattail invasion</li> <li>c. Temporal scale - chronic versus acute toxic effects.</li> <li>d. Spatial scale – small- versus large-scale effects.</li> </ul>
			For some constituents, regulatory criteria or standards do not exist. For these the decision will be made using risk-based action levels.
3 (cont'd)			Confirm that appropriate measurement methods exist to provide the necessary data.  For conventional pollutants, EPA-approved methods are being used to measure environmental variables with an approved QAPP. For some constituents, such as methylmercury in water and sediment, there are no approved and finalized measurement methods.
			Therefore, draft measurement methods are being used for these constituents, with extensive independent QA/QC oversight. MDLs must be: (1) lower than water quality criteria, and (2) low enough to detect spatial patterns and changes from Phase III. In the case of water phosphorus, mercury and methylmercury, MDLs much lower than criterion levels are required.
4	Define the Study Boundaries	<ul> <li>Define the target population of interest and its relevant spatial boundaries.</li> <li>Define what constitutes a sampling unit.</li> <li>Specify temporal boundaries and other practical constraints associated with</li> </ul>	Specify characteristics that define the population of interest. The target population or population of interest is the freshwater marsh of the greater Everglades. The study area includes Everglades National Park, Loxahatchee National Wildlife Refuge, and the Water Conservation Areas (WCAs). The media to be sampled include sediment, floc, water, and biota. The emphasis is on water quality, mercury, habitats and biota. However, one of the desired outcomes of the Project is better estimates of the type and proportion of ecological resources and the impacts of other stressors on these resources in South Florida.  Define geographic area to which decision statement applies.
		sample/data collection.  • Specify the smallest unit on which	The geographic area being studied, and for which decisions apply, is the fresh water portion of the Everglades Protection Area (the public Everglades – the Park, the Refuge, and the WCAs).
		decisions or estimates will be made.	When appropriate, divide the population into strata that have relatively homogeneous characteristics.  Strata of interest were based on the decision statement, rather than on homogeneity of variance. A uniform inclusion probability has been applied throughout the study area for Phase IV.
			Determine the timeframe to which the decision statement applies.  The decision statement applies from the time of the first data collection in the marsh in 1995 through the future. Program results are applicable to an extended timeframe because CERP efforts are projected to occur through 2040. Also,

QAPP FINAL

STEP	DATA QUA	ALITY OBJECTIVES	DESCRIPTION
			phosphorus and mercury control programs will continue indefinitely.
4 (cont'd)		-	Determine when to collect the data.  Because time and space scales are coupled, the synoptic sampling approach spatially dictates that the temporal sampling frequency be seasonal. There are two distinct hydrologic seasons in the Everglades. Generally, the dry season extends from December to May and the wet season extends from June to November. With a Phase IV budget limiting the Program to one seasonal survey, sampling will be done during the wet season because more information is obtainable during the time of year when the entire marsh is flooded.
			Define the scale of decision making.  Decisions on mercury, phosphorus and hydrologic management and restoration issues must be made for the entire Everglades ecosystem.
			Identify practical constraints on data collection.  The large geographic area for sampling, and the need to collect random synoptic samples, require that sampling be conducted by multiple teams using helicopters. Because EPA's budget for contract field support has been reduced, only two helicopters can be utilized in Phase IV. It is estimated that 15 days will be required to reach all 125 sites with only two aircraft. A survey of this length at this time of year in South Florida is vulnerable to tropical storms. The number of samples and sample volume will be minimized to reduce weight and time for collection, while maintaining sufficient volume to attain precision and accuracy requirements. Clean sampling procedures are required for the mercury analyses, both in the field and in the laboratory. Low concentration nutrient analyses also are required because of the oligotrophic condition of native Everglades wetlands.
5	Develop the Analytic Approach	Specify population parameters for making decisions or estimates.     For decision problems, choose a workable Action level and generate and "Ifthenelse" decision rule which involves it.     For estimation problems, specify the estimator and procedure	[NOTE: Environmental stressors in South Florida are not independent; they are often interactive. Multi-media decisions are required for multiple issues. No single statement can be formulated that will permit decisions among alternative actions. The Project, in part, will determine what the criteria should be for multiple issues such as phosphorus loading; water depth, distribution and timing; sulfur; methylmercury concentrations in multiple media, and habitat alteration.]  Specify the statistical parameter that characterizes the population of interest.  The Everglades Ecosystem Assessment is a monitoring and research program, so various statistical parameters have been used to characterize the population of interest. In addition, the emphasis is not on one single constituent, such as a hazardous material that might exceed a regulatory standard.

STE	P DATA	QUALITY OBJECTIVES	Decon
			Rather, several statistical parameters are needed to
			characterize different population attributes, including:
			a. mean and median concentrations of selected
			constituents, as well as cumulative distribution
			lunction curves
	1	1	b. spatial patterns of constituents
			c. spatial/temporal associations among constituents.
.5			Specify action level(s) for the study
(cont'c	d) (t		Several action levels currently exist for phosphorus
			mercury.
		1	1) Phase I control target for total phosphorus of 50
	1	1	I I I I I I I I I I I I I I I I I I I
		1	2) Final control target for total phosphorus of 10
			merograms/L (ppb) (FFA)
			Water total inercury criterion for protection - f
			addatic file of 12 ng/1 (nnt) (EEA CWA)
			5) Proposed predator protection level for mercury of
	1		77 micrograms/kg (ppb) for prey species (CWA).
			Earlier phases of the Program showed that the water column
			The said of the foliage - protective New sight 1
		1	levels are needed, methods with increased sancis:
		1	incoessary. Increased sensitivity is also required to
			puties difficiences and change over time
			statistically significant. In addition TMDI a will be
	1		developed by inodeling, which will require data in a data
			Therefore
			I rogrammatic detection and minimum quantitation is
			Parameters such as water and soil total phooning
			methylmercury and total mercury, and water sulfate are less than the respective criterion.
			Develop a decision rule (an "if then" statement).
	8		Decision rules express what the decision maker ideally
			would like to resolve. The decision has been made it
3			revised citieria are needed based on the information
	li di	1	developed to date from the Program Subsequent:
			1 To Statistically DOOS Will expand and refine decision 1
			additional information becomes available.
			Specify the estimator and procedure.
			The cdf curve, procedures in "R."
		For decision	Identify and define decision errors, choose null hypotheses
6	Specify	problems, specify	and establish the true state of nature for each decision
2022	Performance		by convention, a Type I (false nositive) arror is not
	or		han hypothesis when it is true A Type II (folgo possition)
31.3	Acceptance	• •	of of is not rejecting the nill hypothesis when it is est one
	Criteria	consequences of	two types of decision errors for the Project are
		making incorrect	1. deciding the risk-based action level is exceeded
		decisions from the	when it truly is not  II. deciding the risk-based action level is not exceeded
		The from the	deciding the risk-based action level is not exceeded

owen	DATA QUALITY OBJECTIVES	
6 (cont'd)	test, and place acceptable limits on the likelihood of making decision errors.  • For estimation problems, specify acceptable limits on estimation uncertainty	hypothesis is true.  The true state of nature for decision error (II) is that the null hypothesis is false.  Specify and evaluate the potential consequences of each decision error.  The consequences of deciding that risk-based action levels are exceeded when they truly are not (decision error I) means there will be unnecessary increased control costs associated with nutrient and mercury source reduction, restricted urban and agricultural development, habitat restoration, and restricted hydropattern modification around the natural hydropattern rule curve, which could result in flood damage or water supply shortages. The consequences of deciding risk-based action levels are not exceeded when they truly are (decision error II) means that ecological protection or restoration of the Everglades ecosystem will not be successful.  Establish which decision error has more severe consequences near the action level.  Based on current laws and regulations related to the Everglades ecosystem the decision II error has the more severe ecological consequences near the action level because of the underestimated risk to both ecological and human health and ecological restoration. However, this consequence must be based on a comparative risk assessment and a risk-based benefit/cost analysis of the risks and impacts. The economic consequences are in the billion dollar range for both types of decision errors.  Define the null hypothesis (baseline condition) and the alternative hypothesis, and assign the terms "false positive " and "false negative" to the appropriate decision error. Null hypotheses for DOQs are not equivalent to experimenta
		Establish which decision error has more severe consequences near the action level.  Based on current laws and regulations related to the Everglades ecosystem the decision II error has the more severe ecological consequences near the action level because of the underestimated risk to both ecological and human health and ecological restoration. However, this consequence must be based on a comparative risk assessment and a risk-
		both types of decision errors.  Define the null hypothesis (baseline condition) and the alternative hypothesis, and assign the terms "false positive" and "false negative" to the appropriate decision error.  Null hypotheses for DOQs are not equivalent to experimenta null hypotheses for statistical testing. Null hypotheses for DOQs are not equivalent to experimenta null hypotheses for statistical testing.
		potential consequences. The DQO null hypothesis is equal to the true state of nature that exists when the more severe decision error occurs.  The null hypotheses for this Project, therefore, would be:  Ho =The comparative ecological risk assessment indicates the interactions among stressors puts the South Florida Everglades ecosystem at
		risk.  Ho = The risk-based action levels for nutrient concentrations (10 ppb water, 500 mg/kg soil are exceeded.  Ho = The risk-based action levels for mercury concentrations are exceeded. Ho = The risk-based landscape action level metrics are

STEP	DATA QU	JALITY OBJECTIVES	DESCRIPTION
			exceeded.  Ho = The risk-based action levels for hydropattern modification exceed by X% the natural hydropattern rule curve.  Ho = Phosphorus concentrations are unchanged since the 2005 Phase III sampling.  Ho = Mercury concentrations are unchanged since the 2005 Phase III sampling.
6 (cont'd)			Specify a range of possible values of the parameter of interest where the consequences of decision errors are relatively minor (gray region).  Data from this project may be used to determine action level values. Until these action levels are defined, it is not possible to specify actual numeric values in an area of minor importance. It is, however, possible to indicate that these areas of minor importance will be at the extremes of the distribution. In this portion of the action level curve, there will be a low probability of making either type of decision error.
7	Develop the Plan for Obtaining Data	Compile all information and outputs generated in Steps I through 6 above.  Use this information to identify alternative sampling and analysis designs that are appropriate for your intended use.  Select and document a design that will yield data that will best achieve your performance or acceptance criteria.	The Everglades Ecosystem Assessment Program uses a monitoring design patterned after EPA's National Aquatic Resource Surveys, an outgrowth of EPA's Environmental Monitoring and Assessment Program. It features the Generalized Random Tessellation Stratified design to provide useful information at low cost without compromising reliability. Statistically-based spatial estimates of the magnitude and extent of environmental stressors, as well as statistical detection of change over time for these stressors, are possible with this design. Program data will be analyzed in the "R" survey statistics computer package developed by EPA and others for use on probabilistic data.

### **APPENDIX 2:**

## PROJECT SPECIFIC FIELD SAMPLING METHODS

## A. Bottom water sampling for Sulfide

Samples will be obtained from bottom-most 1 cm of the water column. This zone is equivalent to the nepheloid layer in biogeochemical terms, where reducing conditions are far stronger than they are near the water surface, though theoretically not quite as strong as within the underlying soil pore water. The device designed for this project to accomplish this purpose features a slotted flange that rests on the bottom and an intake point fixed at 1 cm above the flange. Water is drawn through one of several options available to screen or filter the sample to reduce interferences. The option selected will be the one that results in the cleanest sample that is practical to obtain without clogging the device. The intake is connected to tubing that terminates at a three-way valve, to which are attached one syringe for purging the system and another to capture the sample without aerating it. The sampling device is employed as follows.

Place a new filter or screen on the intake area. Attach either short or long tubing (depending on water depth) to the top of the sampler, and attach the syringe assembly (with the side syringe) to the tubing. Attach a new sample syringe (pre-preserved for sulfide analyses) to the end of the assembly (save the cap), and make sure the valve is open towards the side syringe. Slowly lower the sampler to the sediment surface. Use the side syringe to purge air from the tube. Once water is being drawn into the side syringe, switch the valve to the sample syringe and fill it to the 60 mL line. Close the valve, remove the side syringe and tubing, and check the sample syringe for air bubbles. Carefully push any air bubbles out, then cap the syringe and place it back in the long carrying case. Place the filter/screen in the station trash bag and drain any water from the tubing.

## B. Periphyton Assessment and Collection:

Quadrat placement. Place a 0.25-m<sup>2</sup> quadrat at a location that is representative of the station in order to assess periphyton cover. The quadrat must be placed within 5 meters of the station point and placement must be random (behind-the-back toss). Take a photograph of the quadrat from as near to nadir as possible, using the camera with polarizer.

<u>Percent cover.</u> Following the Percent Cover Guide provided, visually estimate the total periphyton cover in the quadrat and record as a percentage. Benthic periphyton is included in this estimate.

<u>Periphyton type(s)</u>. Indicate on the data sheet which of the five periphyton categories [benthic, epiphytic (e.g., growing on bladderwort, or appearing as "sweaters" on spike-rush stems), floating calcareous mat, filamentous green, or none] are present by circling Y or N.

Periphyton collection for biovolume estimate (water column periphyton only). Collect all of the floating and epiphytic periphyton in the water column by hand from within the 0.25-m² quadrat. Separate and discard submerged aquatic vegetation by hand during this process. Strip epiphytic periphyton from graminoid stems and leaves directly into a perforated graduated cylinder. The cylinder is perforated with small holes so that excess water may drain. Use a spare soil tub and site water to separate periphyton from bladderwort leaves; then a 600–um sieve, squirt bottle, and rubber spatula to transfer the drained periphyton into the cylinder. Let water drain completely from the cylinder. Record the volume of material in the cylinder as water column periphyton biovolume.

Water column periphyton sample. After the biovolume measurement is taken, homogenize the periphyton material by hand in the tub and fill the specimen cup with the blue lid to the 120 ml line. Place on ice for transport back to the laboratory. If there is < 120 ml in the quadrat and periphyton is abundant at the station, make up the difference with periphyton collected from the immediate vicinity. If epiphytic and floating periphyton were both present in the quadrat, collect them in approximately the same proportions as they were in the quadrat. Rehomogenize if necessary.

<u>Periphyton collection (benthic)</u>. If mat-like benthic calcareous periphyton is present, this mat is sampled in the soil core. Use a ruler to measure the thickness (cm) of the benthic periphyton layer in each of the 3 cores and record on the field sheet. Separate the benthic mat from the surface of the soil and place it in the specimen cup with the white lid.

### C. Macrophyte Collection

<u>Nutrient standing stocks</u>. At the odd-numbered stations, collect the middle 20 cm of a typical leaf from each of three representative sawgrass plants for TN, TC, and TP analysis.

Mercury standing stocks. At every station whose number ends in a "5," collect one representative whole sawgrass plant (including roots) and place it in a zip-lock bag for total mercury and methyl mercury analysis.

Community mapping. In order to map the vegetation in a 1-km $^2$  area centered on the odd-numbered stations, accurate locations of plant communities will be obtained at each site to be used to train computer classification algorithms for use on WorldView-2 (WV2) imagery. At each of the 63 sites a Trimble R8 RTK GPS, which has an accuracy of no less than  $\pm$  10 cm, will be used to collect locations for the plant communities in the area. The community labels for each location will be associated with the spectral data from that location in the WV2 spectral data. These correlations for the entire dataset will then be used to classify the spectral data into vegetation types.

# APPENDIX 3:

# PROCEDURES FOR LOCATING SAMPLING POINTS

## **EVERGLADES REMAP Phase IV** PROCEDURES FOR LOCATING SAMPLING POINTS

## Finding the Point

EAB's Garmin handheld GPS units will be used to navigate to the sampling points. The Crew Chief (or front seat passenger) will navigate, directing the pilot not to land until the aircraft is right over the point, if practical.

There are three kinds of points, defined as follows:

Nominal -- helicopter can land where the GPS unit indicates that the point is (within 5

Shifted -- pilot cannot land on the point due to safety concerns or potential for damage to the aircraft, but can land nearby (see definition of "Rejected" below) .

Rejected -- pilot cannot land within 20 m of the point, and still be in the habitat type that exists at the point. Rejected points are not sampled. These points will be replaced by points from the replacement (oversample) sample sites drawn from the same subarea. Replacement sites will be used in the order that they were drawn (listed). From the air, photograph the site. Fill out a data sheet for the rejected site upon arrival at the next station, noting the reason for the rejection.

## Sampling a Nominal Point

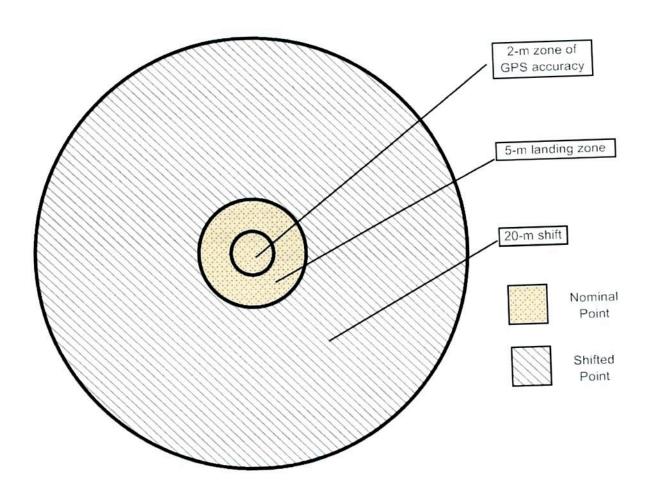
- 1. Land
- 2. Take surface water samples.
- 3. Get sonde readings.
- 4. Zero-out Garmin by walking to point.
- 5. Collect satellite data at the zero point with Trimble unit.
- 6. Take other samples (sediment, floc, periphyton) and readings there.

## Sampling a Shifted Point

- 1. Touch down and then:
  - a. Nudge the aircraft into the habitat of the point, if necessary;
  - b. Move away from the edge, if one is present, unless that is where the zero point is;
  - c. Turn the helicopter so that the left pontoon faces the point.
- 2. Work off left pontoon toward the true point; do not sample the edge unless that is where the zero point is; sample the habitat of the true point.
- 3. Note the shift on the field data sheet.

NOTE: At nominal points, water and sediment are sampled in the same "vicinity". Sampling at the same spot is not possible because of zeroing out the Garmin (steps 4 and 6). However, at shifted points, sediment and water are collected at the same point since there is no need to zero out the Garmin.

## Diagram of a Sample Point



There are 3 concentric circles. All distances are radii. The zone of GPS accuracy is the possible deviation of a perfect landing from the true point, given absolutely no constraints on landing. The landing zone allows for all the many last-moment vagaries of actually getting the helicopter on the ground (5 meters is the approximate length of the aircraft). The shift distance of 20 meters is the maximum allowable and was derived from the combined length of plant sampling transects established in earlier phases of the Program. A nominal point would be anywhere within the inner two circles, whereas a shifted point would be anywhere in the outermost ring.

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9/19/2013

#### **Considering Bias**

No bias is introduced when the helicopters land on the station points, which are randomly drawn. The landing procedure is designed to preserve randomness by relying on the random nature of the motion of a helicopter as it descends the last several meters to the ground. By directing the pilot to go to the point, the random design is preserved. In cases where a safe landing within 20 meters of the point is not possible (such as due to the presence of trees), the point is rejected and replaced by an oversample point, which is also randomly drawn. In that case, the entire habitat at the rejected point is considered non-target. However, where landing at a point is unsafe (such as due to shrubs within a matrix of tall grass), the point is shifted but not rejected if a safe landing can be accomplished in that same habitat within 20 meters of the point. Randomness is preserved by using safety as the only factor in the pilot's decision as to where to set the helicopter down. The crew chief must assure that a shifted landing spot is in the same habitat and does not differ from the intended point by anything other than an obstacle that may come in contact with the helicopter.

**APPENDIX 4:** 

SAFETY PLAN

SESD-EAB Field Safety Plan

Surety I fair
Contact: Pete Kalla
Phone Number: (706) 255 9779
es, Water Conservation Areas, Big Cypress
117 Ave Miami FL 33175
REMAP Study
Miami area.
֡

SITE INVESTIGATION TEAM:

PERSONNEL *	RESPONSIBILITIES
	EPA
Pete Kalla	Project Manager
Greg White	Site Safety Officer, Back-Up Crew Chief/Sampler
Dan Scheidt	Associate Project Manager
Jerry Ackerman	Crew Chief/Sampler
Steve Blackburn	Sampler
Todd Bowers	Sampler
Chris Decker	Crew Chief/Sampler
Megan DeJesus	Sampler
Lonnie Dorn	Sampler
Sue Dye	Crew Chief/Sampler
Morris Flexner	Crew Chief/Sampler
Cornell Gayle	Sampler
Linda George	Sampler
Cindy Gurley	Support
Jeff Hendel	Support
Tara Houda	Sampler
Hunter Johnson	Support
Derek Little	Back-Up Crew Chief/Sampler
Jon McMahan	Sampler
Phyllis Meyer	Support
Doug Peters	Sampler
John Ruiz	Crew Chief/Sampler
Kevin Simmons	Crew Chief/Sampler
Eric Somerville	Back-Up Crew Chief/Sampler
	ESAT
Don Fortson	Support
Brian Herndon	Support
Nathan Mangle	Support
Louie Pounds	Support

<sup>\*</sup> All personnel assigned to these work activities must have received, and be current with the relevant environmental, health and safety training, and participate in the EPA's or other EPA-approved medical monitoring program in accordance with OSHA 29 CFR 1910.120 requirements and the US EPA, Region 4 SESD Safety, Health and Environmental Management Program Procedures and Policy Manual (2009 or most recent version). If any of the assigned personnel are not fully trained or current, they will not be allowed to conduct the work until the relevant training is completed.

# PLAN PREPARATION and APPROVALS: (signatures on file)

Prepared by:	Chris Decker	Date:
Branch Chief:	John Deatrick	Date:
SHEMP Designee:	Greg White	Date:

## **EMERGENCY INFORMATION**

### LOCAL RESOURCES:

Emergency Phone Number for Police/Fire Dept.	Phone: 911
Hospital: Kendall Regional Medical Center	Phone: (305) 223-3000

### **OFFICE RESOURCES**:

WORK PHONE	CELL PHONE
(706) 355-8556	
(706) 355-8654	
(404) 562-8700	
(706) 355-8728	
(706) 355-8705	
(706) 355-8774	
	(706) 355-8556 (706) 355-8654 (404) 562-8700 (706) 355-8728 (706) 355-8705

## **EMERGENCY CONTACTS:**

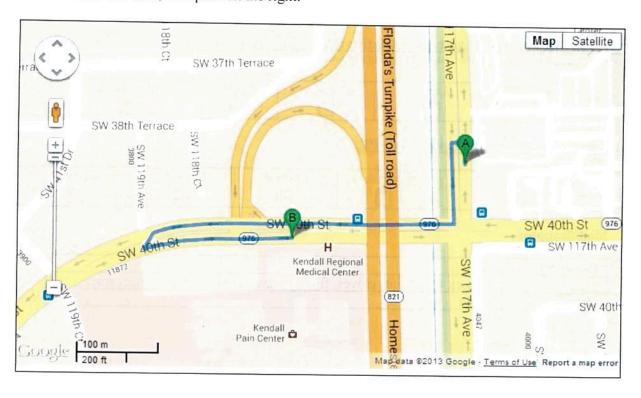
Poison Control Center	Phone: (800) 282-5846
National Response Ctr (ENVIRONMENTAL EMERGENCY ONLY)	Phone: (800) 424-8802

Directions to Hospital: Kendall Regional Medical Center

Kendall Regional Medical Center 11750 SW 40 Street Miami, FL 33175

Hospital is 0.5 miles from hotel.

- Make a U-turn; Hospital on the right.



## Site-Specific Hazards ID/Risks Determination/Controls Assignment:

List hazards that may be encountered ONLY for this work activity (use information from the hazards identification checklist reference included in the Work Control Planning Document)

Hazards	Quantity, Length and/or Likelihood of Exposure	Severity of Exposure or Potential Injury/Illness	Assign Controls	Relative Risk with Controls
Helicopter Flight	moderate	High	Daily flight briefing; safety training; OAS Flight Following	Moderate
Working in extreme temperature conditions	moderate	first aid	ppe / engineering / training	moderate
Poisonous insects, plants; dangerous animals	moderate	first aid	ppe / training/ engineering	moderate
Slip/trip/falls – traversing mountainous or other undeveloped terrain or aquatic systems	moderate	first aid	ppe / engineering	moderate
Driving/travel	moderate	first aid	administration / training	moderate

Overall Site and Work Activities Relative Risk Level: (Based on the hazard/risk determinations above and in the general Work Control Planning Document)

Very Low	Low	Moderate	High	Very High
		✓		

## Recommended General Level(s) of PPE:

Level of Protection:	Level A	Level B	Level C	Level D
(check those that apply)				<b>▽</b>

#### **Modifications:**

Respiratory:	None
Field Dress:	Nomex flight suit, gloves, flight helmet, chest waders as necessary.
Other:	None

# SIGNATURE SHEET\* (signatures on file)

I have read and understand the FSP, and the associated operational controls. I affirm that I will work safely and

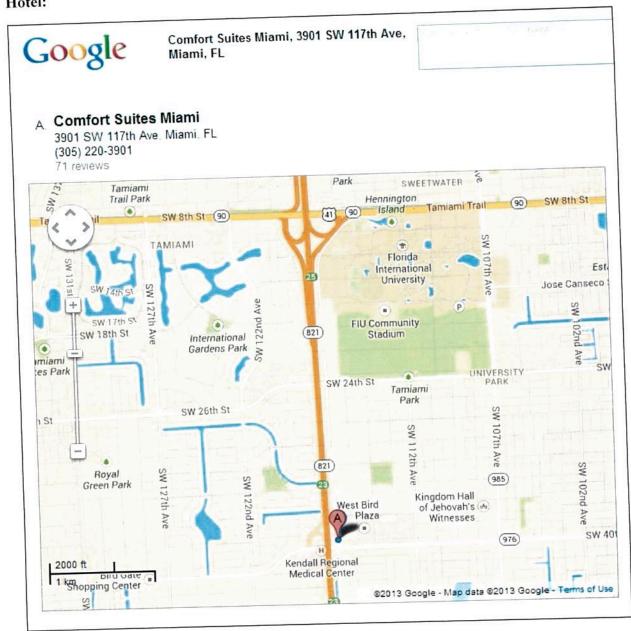
Print Name	Signature	Date
Jerry Ackerman		
Steve Blackburn		
Todd Bowers		
Chris Decker		
Megan DeJesus		
Lonnie Dorn		
Sue Dye		
Morris Flexner		
Don Fortson		
Cornell Gayle		
Linda George		
Cindy Gurley		
Jeff Hendel		
Brian Herndon		
Tara Houda		
Hunter Johnson		
Pete Kalla		
Derek Little		
Nathan Mangle		
Jon McMahan		
Phyllis Meyer		
Doug Peters		
ouie Pounds		
ohn Ruiz		
Dan Scheidt		
Kevin Simmons		
Eric Somerville		
It is recommended that the		

It is recommended that the Field Safety Plan be reviewed prior to mobilizing and again in the field before initiating the work. Personnel should sign following the Field Safety Plan review.

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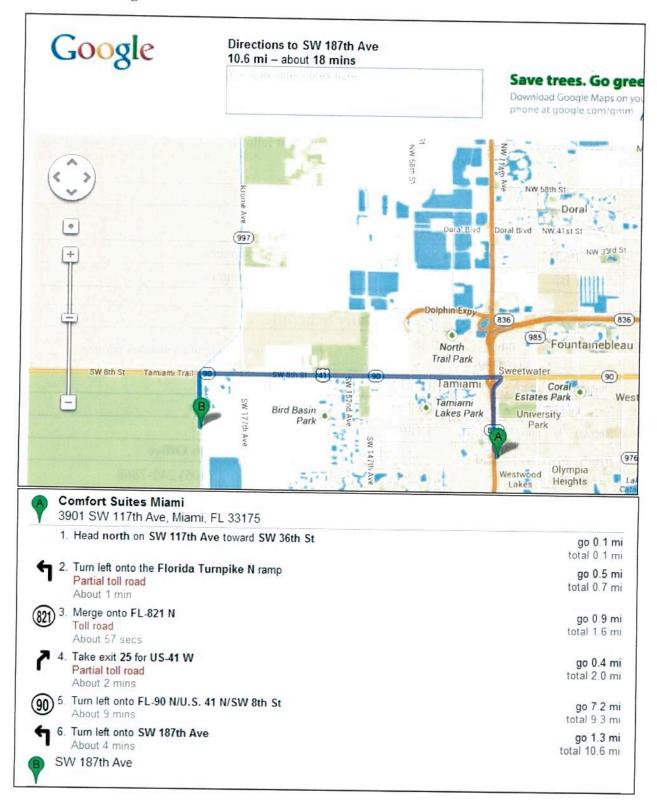
#### **MAPS**

#### Hotel:



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### **Hotel to Landing Zone:**



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### FLIGHT OPERATIONS PLAN

Two float equipped helicopters will be used to reach remote locations in southern Florida within the Everglades National Park and nearby Water Conservation Areas. The two helicopters will operate independently of one another. Daily pre-flight/post flight briefings will be held to discuss safety issues and operating plans for the day.

Flight Following/Tracking will be coordinated by the Everglades National Park Dispatch office and will involve fifteen minutes check-ins along with automated flight following. Pilots will advise the dispatch office when preparing to land and estimate the ground time.

Aircraft				
Туре	Registry Number	Passengers		
Bell 206 B3	N206RW	1 pilot + 3 passengers		
A-Star B2	N351FW	1 pilot + 4 passengers		

	Dail	y Schedule		
Depart From: Landing Zone off 187 <sup>th</sup> Ave (see map)		Destination: anticipate 4 stations per day		
Departure Time:	0730			
Expected to Return by:	1700			
Return No Later Than:	1800			
Flight Following and Tracking:	<b>Everglades National Park Dispatch Office</b>			
	Clayton Camblin		(305) 242-7868	

Note: The specific aircraft used in the study may be subject to change due to scheduling.

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# APPENDIX 5:

FIU PLAN OF STUDY

# Regional Environmental Monitoring and Assessment Program (REMAP) IV:

# Greater Everglades Whole-Ecosystem Monitoring and Assessment

Plan of Study

**July 2013** 

Jennifer Richards<sup>1, 2</sup>

Leonard J. Scinto<sup>1,3</sup>

Yong Cai<sup>1,4</sup>

Daniel Gann<sup>2,5</sup>

Guangliang Liu<sup>1,4</sup>

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<sup>3</sup>Department of Earth and the Environment Florida International University Miami, FL 33199

<sup>4</sup>Department of Chemistry and Biochemistry Florida International University Miami, FL 33199

> <sup>5</sup>FIU GIS/RS Center Florida International University Miami, FL 33199

#### Introduction

The southern Florida Everglades is the largest subtropical wetland in the United States. This wetland is integral to the water supply of the heavily-populated south Florida coastal areas, serves as a breeding ground for numerous wading bird species, is the home to the American alligator and the endangered Florida panther, has the largest mangrove ecosystem in North America, and supports high plant, animal and microbial diversity (Davis and Ogden 1994; Lodge, 2010). In addition to its local, regional and national importance, parts of the landscape are internationally recognized as a RAMSAR Wetland of International Importance, a UNESCO World Heritage Site and an International Biosphere Reserve (Davis and Ogden 1994). Historically, it covered 1.2 X 106 hectares and was characterized by shallow sheet flow that flowed out of Lake Okeechobee in south central Florida, through a sawgrass plain that further south became a patterned peatland consisting of ridges, sloughs, and tree islands oriented parallel to the direction of flow (Davis, 1994; McVoy et al. 2011; Larsen et al. 2011). Major ecological drivers that determined the unique flora and fauna were the subtropical wet/dry climate, shallow water, nutrient--esp. P--limitation, and major disturbances such as fires, freezes and hurricanes (Ogden et al. 2005, McVoy et al. 2011). This wetland has been greatly modified by anthropogenic activities such as drainage, which has decreased the wetland extent to app. half of it original coverage; compartmentalization, which has divided the once-continuous landscape into sub-compartments; and nutrient input, which has altered the biogeochemical cycling throughout the landscape. In addition, southern Florida will be greatly affected by sea level rise, although the timing and exact nature of these effects are uncertain (Zhang 2010; Saha et al. 2011). The Comprehensive Everglades Restoration Plan (CERP), the largest environmental restoration project in the world, is implementing landscape-scale projects to restore this ecosystem (http://www.evergladesplan.org/). The long-term nature of these projects, as well as the continuing anthropogenic influences, require continued long-term, whole-ecosystem monitoring in order to understand impacts and implement adaptive management responses.

The US EPA Regional Environmental Monitoring and Assessment Program (R-EMAP) has provided landscape-scale biogeochemical and ecological data on the greater Everglades ecosystem through three prior (1995, 1999, 2005) sampling iterations (Stober et al. 1996; Stober et al. 1998; Stober et al. 2001a, b; Scheidt and Kalla 2007). Initial Everglades REMAP

monitoring (1995) grew out of concern about high levels of mercury documented in Everglades fish and birds, with potential impacts on humans (Ware et al. 1990; Spalding et al. 1994; Sundlof et al. 1994; Fleming et al. 1995) and was primarily aimed at documenting Everglades biogeochemical cycling, especially with respect to mercury. Because biotic components of the ecosystem are important both to this cycling and to mercury bioaccumulation, as well as because of concerns about Everglades restoration, the initial R-EMAP sampling was broadened in 1999 and 2005 to include biotic parts of the ecosystem such as periphyton, fish, microinvertebrates, and vegetation (Stober et al. 2001b; Scheidt and Kalla 2007). Although south Florida is the subject of much environmental and restoration-related scientific study, the REMAP sampling is unique in applying the same sampling methods in a statistically valid sampling design throughout much of the remaining wetland ecosystem and in having repeated this sampling at 4 to 6 year intervals from 1995 through 2005.

Changes in ecosystem conditions can occur over decadal scales and manifest themselves in various ecosystem components at differing rates, often determined by ecosystem component turnover times (Childers et al. 2003; Gaiser et al. 2005). Previous iterations of R-EMAP have shown the effect of loading on the spatial variation of ecosystem components, including soil nutrients (Osborne et al. 2011), which ultimately affect periphyton/plant biomass, and dissolved organic matter (Yamashita et al. 2010). In this iteration, ecosystem components of soil, floc, water, periphyton, and vegetation will be analyzed for biogeochemical characterization to determine correlations to Hg cycling, spatial distribution of matter and nutrients, and synoptic temporal changes since 2005. Additionally, because biogeochemical processes (e.g. C-fixation/respiration) determine the source/sink characteristics of wetlands and are largely influenced by hydrology and nutrient availability, the lability of C-stored in the soil and floc will be studied at a subset of sites relative to nutrients and microbial activity across the landscape.

The continuation of Everglades R-EMAP in R-EMAP IV will provide critical data for understanding mercury biogeochemistry. First, based upon data obtained in the previous R-EMAP studies (in particular R-EMAP III), we have developed mass budget models for estimating mass inventory of mercury present in the Everglades and for predicting the fate of mercury entering the system (Liu et al. 2008; Liu et al. 2009; Liu et al. 2011). R-EMAP IV will serve as an important checkpoint for testing, calibrating, validating, and refining these models.

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The mercury data for R-EMAP IV will be used to check our previous model results, which will provide field data-based information with respect to the validity and accuracy of our models and subsequently reveal the directions to take to improve these models. Secondly, the continuation of R-EMAP will provide essential data for understanding the role of some important transport and transformation processes of mercury in the biogeochemical cycling of mercury that were inadequately addressed previously. For example, our previous studies suggested that the uptake, storage, and transport of mercury in macrophytes such as sawgrass could play an important role in determining the fate of mercury (Liu et al. 2011), yet little data (in particular ecosystem-wide data) are available about that potential role. The addition of new components, such as mercury analysis in sawgrass in R-EMAP IV, will complement our understanding of the overall biogeochemical cycling of mercury. Thirdly, the continuation of Everglades R-EMAP will expand the temporal databases, which could enable us to understand temporal changes in mercury for this ecosystem using statistical techniques such as trend analysis.

Previous R-EMAP studies have quantified Everglades vegetation through detailed transect analyses, as well as mapping plant communities around the vegetation from aerial photographs (Stober et al. 2001; Richards et al. 2008; Madden et al. 2008). Building on this prior work, R-EMAP IV will use high resolution, remotely-sensed data to map vegetation around sampled points, then use the maps, plant tissue nutrients and mercury data sampled from mapped sites, as well as data from the literature, to estimate biomass, nutrient and mercury standing stocks for sites distributed across the ecosystem. In addition, vegetation at mapped sites will be compared to 2003/2004 aerial photography of the same sites to understand vegetation trends.

In summary, Florida International University (FIU), in cooperation with the US-EPA and Everglades National Park, proposes to undertake R-EMAP IV in order to sample soil, surface water, floc, periphyton and fish total mercury and methyl mercury throughout the Greater Everglades Ecosystem (GEE); provide a characterization of the biogeochemistry of the same samples; and characterize vegetation at a subsample of these habitats in order to understand the environmental context for biogeochemical changes and mercury transformations throughout the ecosystem. Because R-EMAP IV will be the fourth sampling over the past 18 years, and because half of R-EMAP IV samples will re-visit sites sampled in 2005, this study will build on the prior studies to add a temporal understanding to the R-EMAP whole ecosystem perspective and to

provide information relevant to analyzing trends and informing management of the entire ecosystem.

### Materials and Methods

Data and samples will be collected at each of 125 sites distributed across the greater Everglades ecosystem in the fall, wet season, 2013 (Figures 1, 2). Sampling in this landscape-scale program uses a GRTS sampling design; since all measurements will be obtained at a random sample of locations throughout the system, estimates for all parameters will be statistically valid. Additionally, in this R-EMAP iteration half of the locations sampled will be sites previously visited in 2005, allowing for estimations of change at those sites (Figure 2).

In this cross-agency and -institution collaborative study, US EPA is responsible for conducting the field sampling of water, soil, floc, periphyton, and fish (Table 1). FIU is responsible for providing assistance with staging for the biogeochemical sampling of water, soil, floc, periphyton, vegetation, and fish, will be the lead analytical lab for laboratory analyses of these samples (Table 1), and will analyze and report results. FIU will also be the lead analytical lab for total Hg and methyl Hg samples of water, soil, floc, periphyton, sawgrass and fish (Table 1), and will analyze and report results. Finally, at one-half (63) of the sites FIU will use the field visits to acquire training data to map vegetation using remotely-sensed satellite data for 1 km2 around the sites, sample sawgrass for nutrient analyses at these sites, estimate sawgrass height and density, and sample sawgrass for Hg analyses at a subset of these sites. FIU is responsible for analysis and reporting of these results. For the mapped sites, the FIU group will analyze TC, TN, and TP in sawgrass collected by the FIU vegetation person and will use this information, plus information from the literature, to estimate nutrient standing stocks for sawgrass for those sites and determine how these vary spatially and in relation to environmental and landscape variables. For a subset (25) of the 63 mapped sites the FIU group will also measure total Hg and methyl Hg in sawgrass samples and use these data plus the percent sawgrass cover in the mapped area to estimate Hg standing stocks and analyze their spatial variation. This subset of 25 sawgrass mercury sampling sites will be selected to be distributed throughout the R-EMAP sampling area.

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Field measurements will be done by US EPA during sampling; nutrient and Hg sample analyses, as well as vegetation sampling, will be done by FIU. A summary of sampled parameters and variables follows; additional details and responsible parties are given in Table 1.

Hydrology and Water Quality: water depth, dissolved inorganic nutrients, dissolved organic C, TP, TC, TN, and chlorophyll a contents.

Soil and Floc Quality: soil and floc type, thickness, bulk density, mineral content, AFDW, pH, TP, TC and TN. FIU is responsible for laboratory soil nutrient analyses. A subsample of 25 spatially distributed sites will additionally be analyzed for CO2 generation and total inorganic C (TIC) content to determine stability of stored C; these samples will be selected after sample collection and will be partitioned between ridge (sawgrass) and slough (water lily) habitat.

Mercury Contamination: MeHg and THg in surface water, soil, floc, and periphyton; THg in whole-body mosquitofish. Additionally THg and MeHg in sawgrass sampled from 25 spatially distributed sites; these will be sites where sawgrass TC, TN, and TP is also being determined and for which vegetation is being mapped.

Habitat Quality: vegetation mapping using WorldView-2 satellite data (2x2 m pixel resolution, 8 spectral bands) for 1 km2 centered on the sampling site location for ½ (63) of the sites. A sample of sawgrass leaves at each of these sites will be collected and analyzed for TC, TN, and TP, and sawgrass height and density will be estimated.

Ecosystem Integrity: periphyton cover, bio-volume, biomass, dry weight, AFDW, Chlor a and CNP ratio of periphyton; additionally, periphyton cover for the 1 km2 around the site location will be estimated in the vegetation mapping.

## Water and Soil Biogeochemistry Materials and Methods

#### Objectives:

 To determine spatial distributions in soil, floc, periphyton, vegetation and water biogeochemical characteristics across the GEE and to compare changes since the 2005 sampling.

- To correlate biogeochemical parameters to vegetation/periphyton biomass and mercury models, especially to inform influences due to hydrology and/or nutrients.
- To spatially determine ecosystem characteristics along natural or man-made gradients in hydrology to inform projections of potential changes due to system-wide restoration activities.

Field sampling will be conducted by the US EPA with samples returned to the FIU campus for logging and distribution to several laboratories responsible for sample analysis. The Southeast Environmental Research Center (SERC) Nutrient Analysis Laboratory (NAL) will analyze water samples for soluble reactive orthophosphate (SRP; US EPA method 365.1), and total phosphorus (TP; US EPA 365.1, following dry ashing according to Solorzano and Sharp 1980), soluble nitrate, nitrite (NO3, NO2; US EPA 353.2) and ammonium (NH4; US EPA 350.1) on an automated colorimeter. Water total nitrogen (TN: ASTM D5176) and total and dissolved organic C (TOC; US EPA 415.1) will be determined on a Shimadzu TOC-VCSH fitted with a Shimadzu TNM-1 Total Nitrogen Analyzer. Chorophyll a contents of water (field filtered), floc and periphyton (subset of samples) will be fluorometrically analyzed after 90% acetone extraction (SM 10200H; APHA 1998 - modification as per QAP). The SERC NAL will also analyze TP in all solid materials (soil, floc, periphyton, plants, etc.) by dry ashing/colorimetry as above, and, where appropriate (e.g. periphyton), will analyze extracted Chlor a. The SERC NAL is NELAC Certified (Certification # E76930) for General Chemistry (dissolved and total nutrients in fresh and salt waters), Chlorophyll a and Total P in solids and tissues. Soil, floc and tissue (vegetation and periphyton) samples will be analyzed for all parameters other than TP and Chlor a by the SERC Soil/Sediment Biogeochemistry Laboratory (SBL). The SBL does not have NELAC certification. However, the laboratory maintains strict Quality Assurance and Quality Control procedures. Soil, floc and tissues will be weighed for total wet and dry weights (after drying at 80° C until constant weight) to determine bulk density and percent moisture. Subsamples will be combusted in a muffle furnace at 550° C for 3 h to obtain ash content and organic matter (Ash-free dry weight (AFDW)) by loss on ignition (ASTM D2974-87) Soil, floc and plant tissues and periphyton samples will undergo analysis for TC (TIC if applicable), and TN. Total inorganic C is determined by conducting the TC analysis on

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ashed material (see above for ash content). Solid samples will be analyzed for total C and N using a Carlo-Erba Flash EA 1112 (Nelson and Sommers, 1996).

The stability or lability of organic matter in soil or floc will be determined using a vial assay where nominally 4.5 g subsamples of fresh weight soil/floc are mixed in a 1:1 ratio with an equal mass (g-1) of distilled deionized water (DDIH2O); this mixture will be incubated for a known duration between 24 - 78 h in 20 mL headspace vials purged with CO2-free air. After incubation, the headspace will be analyzed for CO2 production using a Hewlett Packard 5890 Series II Gas Chromatograph (GC) fitted with an automated headspace sampler (HP-7694). Carbon-dioxide will be converted to CH4 via a methonizer (Ni catalyst and H2 gas stream, Shimadzu MTN-1) at 450°C (Amador and Jones 1992, Amador and Jones, 1995) and analyzed by flame ionization detection (FID) following retention on a HEYASEP-R column (Alltech, Inc.). Peak area will be interpolated by ELAB software version 4.02R and calibrated based on a standard curve of known gas concentrations.

# Mercury Biogeochemistry Materials and Methods

#### Objectives:

- To provide an improved, comprehensive understanding of the biogeochemical cycling of mercury at the watershed scale in the Everglades.
- To utilize the data of this sampling iteration to test, validate, and redefine the mercury
  mass budget models developed based on the previous R-EMAP data to more
  accurately predict the fate of mercury in the Everglades wetland ecosystem.
- To provide in-depth information on important mercury transport and transformation processes that were inadequately addressed previously.

The Mercury Laboratory at SERC (SERCMLAB) will undertake the task of mercury analysis (including methyl and total mercury) and provide assistance to US EPA sampling teams. As a laboratory accredited by the National Environmental Laboratory Accreditation Conference (NELAC) for analysis of mercury (total and methyl) and a variety of metals in water, solid, and biological samples, SERCMLAB follows the Standard Operating Procedures (SOPs) developed based on the approved US EPA methods and complies with comprehensive quality assurance

and quality control (QA/QC) requirements. The water, soil, floc, periphyton, fish, and plant samples, collected based on a probability sampling design and using clean sampling techniques, will be transferred to the laboratory on the same day of sampling. Water samples will be acidified inside a clean room and stored in the dark at room temperature until analysis (usually within 14 days for MeHg and 28 days for THg). Soil, floc, periphyton, fish, and plant samples will be stored in the freezer before analysis (generally within 28 days). The laboratory procedures for sample treatment and analysis are briefly described below and detailed information can be found in the complete SOPs.

Determination of total mercury. Total mercury analysis will be performed following the SOPs modified after US EPA methods 1631 for water and 7474 for soil, floc, periphyton, plant, and fish. Water samples will be subject to UV-brominating digestion before cold vapor atomic fluorescence analysis (CV-AFS). Soil, floc, periphyton, and plant samples will be first homogenized with a blender and acidified by adding 10% HCl to release CO2, as these samples are not homogenous and some of them contain high concentrations of carbonate. After homogenization, samples will be placed in ampoules and digested with concentrated HNO3 at 105 ?C for 1 h using an autoclave. After digestion, the samples will be cooled to room temperature and diluted for THg analysis. For mosquito fish, the entire fish will be weighed into an ampoule and the same digestion procedures using HNO3 will be followed. For each site, up to 7 fish will be analyzed and the average and weight-adjusted THg will be reported.

Determination of methyl mercury. Determination of MeHg in water, soil, floc, periphyton, plant, and fish samples will be conducted following the SOPs modified after US EPA methods 1630. Water samples will be distilled first to isolate MeHg from the matrix, and the distilled samples will be subject to an aqueous ethylation - purge and trap - gas chromatograph separation - AFS detection procedure for MeHg analysis. Ethylation will be performed by adding 2 ml of acetate buffer (2M) and 0.2 ml of 1% NaBEt4. After 15 min of ethylation, a Tenax trap will be connected to the bubbler which will then be purged for 15 min at 200 ml/min of N2 flow to collect ethylated MeHg onto the trap., The trap will be dried for 3 min under 200 ml/min of N2 and analyzed. MeHg in the homogenized soil, floc, periphyton, and plant samples will be isolated by an acidic KBr/ H2SO4/CuSO4 (1.5/1.8/1 M) solution, followed by extraction of MeHg into the organic layer with CH2Cl2. Two ml of CH2Cl2 extract will be

9/19/2013 SESD Project ID: 13-0513 pipetted into a 50-ml plastic vial containing 40 ml of reagent blank water. The vial will be placed in a water bath at 45 ?C and purged with N2 at flow rate of 100 ml/min for 30 min to completely volatilize CH2Cl2, leaving MeHg in the aqueous solution. The aqueous solution will be transferred into a bubbler with a four way stopcock for ethylation - purge and trap - GC-AFS analysis of MeHg.

Quality Assurance of Hg Analysis. Strict quality assurance and quality control procedures will be followed during sample analysis. At least two method blanks, a pair of matrix spikes and/or two certified reference materials (CRMs) will be included in each sample batch (up to 20 samples). All method blanks need to be below the corresponding detection limits (THg: 0.2 ng/L for water, 2.4 ng/g for soil, floc, and periphyton, 3.2 ng/g for mosquitofish; MeHg: 0.02 ng/L for water, 0.04 ng/g for soil, floc, and periphyton). Recoveries for all matrix spikes or CRMs need to be within the acceptable ranges specified in the SOPs (70-130% for THg and 65-135% for MeHg). The performance of the instrument will be checked by running an intermediate calibration standard at regular intervals (usually every 10 samples), and all continuing checks need to be within the acceptable range (85-115% for THg and 67-133% for MeHg, compared to initial readings). Sample analysis will be monitored for complying with the QA/QC requirements and immediate measures, including investigation of causes, corrections of procedures, and/or reanalysis of samples, will be taken in the cases where QA/QC requirements are not met.

An array of data mining and data analysis techniques will be employed to comprehensively analyze the mercury results, in combination with soil/water biogeochemical and vegetation data. The data will be used for checking the model results previously obtained in our mercury mass budget models. The models will be adjusted and redefined by optimizing the input parameters and/or including new mercury transport and transformation processes. The data will be analyzed to provide an improved understanding of not only the overall picture of mercury cycling in the system, but also some specific mercury transport and transformation processes.

## Vegetation Sampling and Mapping

#### Objectives:

- To provide the vegetation context for the R-EMAP biogeochemistry samples and integrate the biogeochemical data with vegetation composition and other environmental parameters.
- To estimate sawgrass standing stocks of TC, TN, and TP and determine how these vary on a landscape scale.
- To estimate mercury standing stocks in sawgrass and determine how these vary on a landscape scale.
- To compare 2013 vegetation around R-EMAP IV sampling points to 2003/2004 aerial photography for the same points to analyze vegetation trends.

We will create 1 km2 maps around half (63) of the R-EMAP IV sampling points, distributed throughout the R-EMAP region of interest; which points we map will depend on Digital Globe's WorldView-2 (WV2) satellite data availability. WV2 spectral data has 8 bands (5 in the visible, 3 in the near infra-red; we use 7 of these for vegetation mapping) and a 2x2 m spatial resolution. We have used these data to successfully map plant communities in Northeast Shark Slough in Everglades National Park and in southern parts of Water Conservation Areas 3A and 3B (Gann et al. 2012). Half of the points mapped in R-EMAP IV will be new sites, while half will be sites mapped in the 2005 R-EMAP sampling. We will acquire WV2 satellite imagery for a 1 km2 area centered on each of the 63 R-EMAP IV sampling points. We currently have WV2 satellite data for most of Everglades National Park and the southernmost area of WCA 3. We have examined the Digital Globe archives and know that archived images are available for the other R-EMAP areas. The WV2 satellite was launched in 2009, so all images will be more recent than 2009, but we will use archived images from multiple dates from 2009 to 2013.

In order to map vegetation, we will obtain accurate locations of plant communities at each site to be used to train computer classification algorithms. At each of the 63 sites we will use a Trimble R8 RTK GPS, which has an accuracy of no less than  $\pm$  10 cm, to collect locations for the plant communities in the area. The community labels for each location will be associated

9/19/2013 SESD Project ID: 13-0513 with the spectral data from that location in the WV2 spectral data. These correlations for the entire dataset will then be used to classify the spectral data into vegetation types. Additionally, we will collect two types of photographic documentation to help in vegetation training. At each of the sites, we will photograph vegetation in all directions from the helicopter pontoons, creating a 360o record for the site. We will also mark the sampling point on the ground with a bio-degradable marker and photograph the point and surrounding vegetation from the air on take-off. These photographic records will provide additional training information.

The WV2 images will be georectified and then atmospherically corrected using ENVI's Fast Line-of-sight Atmospheric Analysis of Spectral Hypercubes (FLAASH) algorithm (ITT\_Visual\_Information\_Solutions 2009). We will classify vegetation with supervised classification algorithms using the training sample data collected from each sampling site. Vegetation community classes will be based on our previous experience using WV2 data in the Everglades (Gann et al. 2012). Accuracy and confidence estimates will be determined for the classification process (model-based) and overall and class-specific accuracies for the final maps (design-based). The mapping is an iterative process of training set selection, classifier construction, classifier evaluation, classification of all map units, visual evaluation of the map, acquisition of additional training points, and re-classifying. Finally, when model-based accuracies and visual evaluation of maps are acceptable, the final map will be evaluated based on a stratified random sample by class and will be validated using aerial photography, including stereo imagery. To read, process and analyze spatial vector, raster and table data, we will use the {rgdal}, {raster}, {maptools} packages in R (R Core Team 2013). To classify, we will use the randomForest function from the {randomForest} (Liaw and Weiner 2002) package in R. For the accuracy assessment we will use the R packages {sampling} and {e1071} (Cohen 1960; Hubert and Arabie 1985).

During the field sampling, we will collect sawgrass samples for nutrient analyses at 63 sites. Three recently mature, healthy sawgrass leaves, one from each of three culms, will be collected. Total C, TN, and TP will be determined for these samples (see Water and Soil Biogeochemistry Materials and Methods, above). Using the sawgrass nutrient data, literature values for above- and below-ground biomass for sawgrass (e.g., Serna et al. (submitted) and references therein), and percent sawgrass cover from the maps, we will estimate total C, N and P

sawgrass standing stocks for each km2, and determine how these vary across the landscape and with other environmental and landscape variables measured.

Mao et al (submitted) have recently found that > 90% of total mercury in sawgrass leaves was obtained from atmospheric mercury, indicating that understanding mercury concentrations in sawgrass and how it varies across the landscape is important to understanding mercury standing stocks and transformations for the whole ecosystem. To estimate standing stocks, FIU will collect sawgrass samples from 25 of the mapped sites, targeting sites that are dominated by sawgrass and that are spatially distributed. A single small to medium-size plant, including roots, stems and leaves, will be collected at each site. Total mercury and methyl mercury will be determined for these samples (see Mercury Biogeochemistry Materials and Methods, above). Using analyses similar to those for TC, TN, and TP, we will estimate mercury standing stocks from the measured total and methyl mercury concentrations, above- and below-ground biomass for sawgrass, and percent sawgrass cover per km2 as determined from the vegetation maps. These data will show how mercury standing stock varies among sites, adding a spatially explicit component to Everglades sawgrass mercury budgets.

Finally, for R-EMAP sites sampled in both 2005 and 2013, we will visually compare the newly acquired vegetation data to 2003/2004 aerial photography around the same area in order to analyze large-scale trends in vegetation. These data will allow us to understand how much of the Greater Everglades landscape has changed and to determine the types and spatial distribution of those changes.

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Table 1. Environmental media, parameters and analytes, and participating organizations for R-EMAP IV.

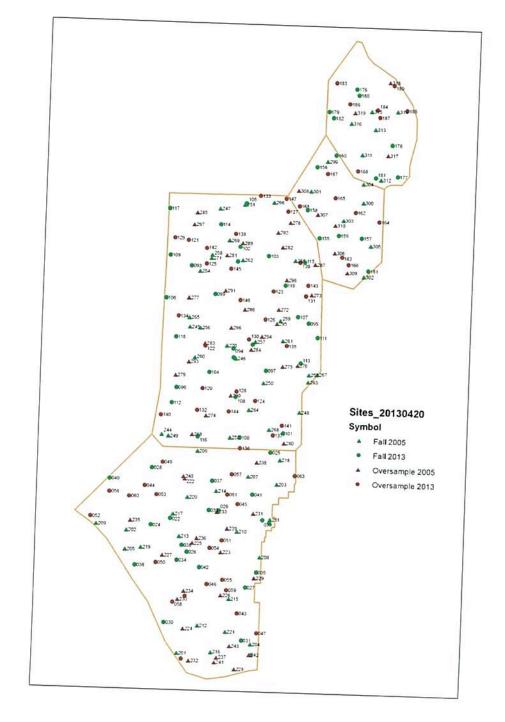
Medium	Parameters and Analytes	Field- measured or Sampled by	Analyzed by
Surface Water	DO, Cond., pH, Temp., Turbidity, Depth	EPA	
	TP, TC, TIC, TN, chlorophyll-a	EPA	FIU
	Dissolved: NH <sub>4</sub> , NO <sub>2</sub> , NO <sub>3</sub> , PO <sub>4</sub> DOC, SO <sub>4</sub> , Cl, THg, MeHg	EPA	FIU
	boc, so4, ci, ring, Meng	EPA	EPA
Bottom Water	H <sub>2</sub> S	EPA	FIU
Soil		EPA	EPA
3011	Type, Thickness pH	EPA	
	The state of the s	EPA	EPA
	Bulk Density, AFDW, Mineral Content	EPA	FIU
	TP, TN, TC, TIC, CO <sub>2</sub>	EPA	FIU
Floc	THg, MeHg, methane	EPA	FIU
rioc	Bulk Density, AFDW, Mineral Content	EPA	FIU
	TP, TN, TC, chlorophyll-a, methane, CO <sub>2</sub>	EPA	FIU
Doninketse	THg, MeHg	EPA	FIU
Periphyton	THg, MeHg, BD, AFDW, C:N:P, chl-a	EPA	FIU
	Cover, Volume Mass	EPA	
Maaaa: 4-6-1		EPA	FIU
Mosquitofish	THg	EPA	FIU
Plant Community Mapping	Vegetation training samples at 63 sites, classified by Everglades Vegetation Classification System and located to submeter accuracy	FIU	
Sawgrass	Sawgrass leaf C:N:P at 63 sites; THg, MeHg in sawgrass at 25 sites:	EPA	FIU

Figure 1. Southern Florida R-EMAP IV study area (2098.6 sq. mi.) outlined in orange.



# Figure 2. Everglades Ecosystem Assessment Phase IV sites.

The Fall 2005 sites are a random subsample of half of the R-EMAP III (2005) wet season sites, included for change detection purposes. The Oversample sites are extras to be used as replacements for sites that cannot be sampled for various reasons, usually because they fall in or immediately adjacent to a tree island, or in an upland habitat, or because woody vegetation is too dense to enable a safe helicopter landing and take-off.



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